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## (54) ARAGONITIC PRECIPITATED CALCIUM CARBONATE PIGMENT FOR COATING ROTOGRAVURE PRINTING PAPERS

AUSGEFÄLLTES ARAGONIT KALCIUMKARBONATPIGMENT ZUR BESCHICHTUNG VON  
TIEFDRUCKPAPIEREN

UTILISATION D'UN PIGMENT DE CARBONATE DE CALCIUM ARAGONITIQUE PRECIPITE POUR  
LE COUCHAGE DE PAPIERS D'IMPRESSION A ROTOGRAVURE

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(56) References cited:  
**EP-A- 0 768 344** **GB-A- 1 500 697**  
**GB-A- 2 139 606** **US-A- 5 120 365**

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**Description****BACKGROUND OF THE INVENTION**

## 5    1. Field of the Invention:

[0001] This invention relates to a technique for the union between an aluminum profile and a resin material, and more particularly to resin-composite aluminum profiles having a resin material joined to an aluminum profile, especially heat insulating aluminum profiles having the joined parts of opposed lateral sheet members of an aluminum profile  
10    formed with a resin material, a method for the production of the profiles, and an apparatus, particularly a discharge treatment apparatus to be used for the production of the profiles.

[0002] The term "aluminum profile[s]" is used herein to express the shapes or sections of aluminum or an aluminum alloy shaped into a continuous form (hereinafter referred to simply as "profile[s]") and the term "resin-composite aluminum profile[s]" is used to express the concept embracing the heat insulating aluminum shapes or sections (hereinafter referred to simply as "heat insulating profile[s]").  
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## 2. Description of the Prior Art:

[0003] The composite profiles having a resin material joined to the surface or recess of a profile have been used in various technical fields because they are light and excellent in durability, strength, or the like. Particularly, in the technical field of construction, sashes which are provided on either of the exterior and the interior side of building with a double paper sliding door disposing part have been disseminating with a view to affording insulation from heat, abating noise, and preventing dew condensation. The heat insulating profiles are used in the frames of such sashes.  
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[0004] The heat insulating profile is provided between the opposed lateral sheet members thereof with a joined part formed of synthetic resin and, in this structure, allowed to have the opposed lateral sheet members integrally joined by the adhesive force of the resin material and, owing to the intervention of the resin material between the opposed sheet members, enabled to manifest the functions of affording insulation from heat, abating noise, and preventing dew condensation. As the resin material mentioned above, generally a foamable hard polyurethane resin is used as taught in published Japanese Patent Application, KOKAI (Early Publication) No. 54-19,537, for example.  
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[0005] Generally in the production of the heat insulating profile, a urethane resin material is injected to capacity into a recess provided between the coated, opposed lateral sheet members of a profile and wished to be packed with a resin and thereafter the portion of the profile which forms the recess is cut so that the opposed lateral sheet members are joined to each other solely with the urethane resin.  
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[0006] Since the adhesive force produced by the urethane resin is not sufficient, however, the resin and the profile are liable to peel off each other. Once the separation of this sort occurs, the profile has the problem of emitting a squeak when deformed under an external force and betraying deficiency in strength as well. Further, the heat insulating profile entails the problems of durability such as causing shrinkage of the urethane resin after a protracted use, tending to induce the phenomenon of giving rise to a step in the butt end (discernible by a test of repeating cycles of cooling and heating), and possibly inserting a crack in the face of union and inducing leakage of rain water through the crack. For the purpose of compensating the urethane resin for the shortage of adhesive force, such measures as applying a primer layer to the inner surface of the recess in the profile wished to be filled with resin or mechanically forming a multiplicity of claw parts on the inner surface have been heretofore proposed. These measures, however, entail highly expensive treatments, require introduction of expensive devices, and suffer poor productivity. These treatments are not easily performed uniformly on the inner surface of the recess, particularly so when a hole-forming part for a screw  
40    is protruding into the recess. Further, methods and devices, as specified in the precharacterizing portions of appended claims 1 and 10, respectively, are disclosed in US-A-3 451 871 and EP-A-0 372 634.  
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**SUMMARY OF THE INVENTION**

[0007] It is, therefore, an object of the present invention to develop a technique for improving the adhesive force to be generated between a profile and a resin by a relatively simple and inexpensive method and, therefore, allow manufacture of the composite profiles or heat insulating profiles having a profile and a resin joined fast to each other at low cost with high efficiency.  
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[0008] Particularly, the present invention has for an object thereof the provision of the composite profiles, especially the heat insulating profiles, which allow easy treatment of the recess wished to be filled with resin even when a hole-forming part for screw is protruded into the recess, produce high adhesive strength between a profile and a resin, prevent the profile from emitting a squeak even on exposure to an external force, exhibit high strength, offer strong resistance to the shrinkage of resin, entail virtually no phenomenon of giving rise to a step in the butt end, and excel  
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in durability enough to withstand a protracted use and a highly efficient method for the manufacture thereof.

[0009] A further object of the present invention is to develop an apparatus, particularly an electrode for a discharge treatment apparatus, which can be advantageously used for the method described above.

5 [0010] To accomplish the objects described above, the present invention in the basic aspect thereof provides a method for the production of a resin-composite profile as specified in appended claim 1. When the profile has a recess wished to be packed with resin, the discharge treatment is performed on the inner surface of the recess and the discharge treated recess is filled with the resin material.

[0011] The adoption of this method equals the provision of a resin-composite profile which has a resin material joined fast integrally to the discharge treated portion of the coated surface of the profile.

10 [0012] The profile to be effectively used for the present invention may be a profile having a coating film formed by a coating treatment on the surface of a profile of aluminum or an aluminum alloy, generally an extruded profile, or a profile having formed thereon a composite film comprising an anodic oxide film, colored oxide film, or chemical conversion film and a coating film superposed thereon. Thus, a profile furnished on the surface thereof with a coating film is invariably usable for the present invention. The coating treatment involved herein may be performed by any of the heretofore known methods such as, for example, electrodeposition coating, immersion coating, and electrostatic coating.

15 [0013] In accordance with another aspect of the present invention, there is provided a method for the production of a heat insulating profile characterized by performing a discharge treatment on the inner surface of a recess disposed between opposed lateral sheet members of a coated profile and intended to be filled with resin, filling a resin material in the discharge treated recess, and then cutting the portion of the profile forming the recess, thereby obtaining a heat insulating profile having the opposed lateral sheet members integrally joined to each other with the resin material filled as described above. When the profile mentioned above has at least two recesses disposed between the opposed lateral sheet members and destined to be filled with resin, the discharge treatment and the packing of resin material are performed on the interior of one of the recesses and then the portion of the profile forming the other recess is cut when the portion of the profile forming the recess mentioned above is subsequently cut, a resin sheet is superposed on the cut portion of the other recess to occlude this cut portion, and subsequently the discharge treatment and the packing of resin material are performed on the interior of the other recess, as specified in appended claim 3.

20 [0014] The adoption of this method results in the provision of a heat insulating profile which has the joined part of the opposed lateral sheet members of a coated profile, the joined part (joining member) being formed of a resin material joined fast integrally to the discharge treated portions of the opposed surfaces of the opposed lateral sheet members.

#### BRIEF DESCRIPTION OF THE DRAWINGS

35 [0015] Other objects, features, and advantages of the invention will become apparent from the following description taken together with the drawings, in which:

Figs. 1A through 1F are schematic explanatory diagrams illustrating a process for producing a heat insulating profile according to the method of the present invention;

40 Fig. 2 is a fragmentary perspective view illustrating one example of an aluminum sash formed by assembling heat insulating profiles of various structures;

Fig. 3 is a fragmentary cross section of a heat insulating profile having a hole-forming part for a screw;

Fig. 4 is a cross-sectional view illustrating the state in which an electrode for discharge treatment is inserted into a pouring pocket in the lower frame;

45 Figs. 5 through 9 are perspective views illustrating various kinds of electrode; Fig. 5 depicting an electrode shaped like a round rod, Fig. 6 an electrode shaped like a plate, Fig. 7 an electrode shaped like a disc; and Fig. 8 and Fig. 9 electrodes of other shapes;

Fig. 10 is a fragmentary perspective view illustrating one example of a device for corona discharge treatment;

Fig. 11 is a perspective view illustrating one example of a device for adjusting the position of an electrode;

50 Fig. 12 is a fragmentary perspective view illustrating the state in which an electrode shaped like a plate is inserted into a pouring pocket of a profile;

Fig. 13 is a fragmentary perspective view illustrating the state in which an electrode shaped like a disc is inserted into a pouring pocket of a profile;

Fig. 14 is a partially sectioned perspective view illustrating the state in which resin is being poured into a pouring pocket of a profile;

55 Figs. 15 through 17 are graphs showing changes of the amount of functional groups in the surface of a coating film before and after various coated profiles have undergone a discharge treatment; and

Fig. 18 is a graph showing the change of the ratio of shrinkage of urethane resin found by a test of repeated cycles of cooling and heating performed on various kinds of heat insulating profiles.

## DETAILED DESCRIPTION OF THE INVENTION

[0016] The production of a composite profile or heat insulating profile according to the present invention is basically characterized by increasing the adhesive strength between resin and a profile by performing a discharge treatment in advance on the coated surface of the resin-joining portion of a profile or the coated inner surface of a recess formed in the profile and destined to be packed with resin. When the discharge treatment of this sort is performed, the chemical bonds between the resin molecules forming a coating film on the surface of the profile are severed and free hydrophilic functional groups such as, for example, -OH, -COOH, =NH, -NH<sub>2</sub>, -SH, -SOH, or -NHCO- are formed, depending on the kind of coating material used, by the discharge energy or liberated electrons, with the result that the resin on the surface of the coating film will acquire improved wettability. It is also conceivable that the ozone generated by electric discharge will activate the surface of the coating film and improve the affinity of the surface for the resin. These actions markedly exalt the adhesive strength between the resin and the profile and, even in the heat insulating profile of a structure such that the opposed lateral sheet members thereof are joined to each other solely with a resin material interposed therebetween, allow integral union with markedly high adhesive strength. The heat insulating profile itself, therefore, acquires enhanced strength, avoids emitting a squeak on exposure to an external force, offers high durability to resist the shrinkage of resin during a protracted use, and entails virtually no possibility of forming a step in the butt end. Particularly, when the resin material to be used for filling is such a resin as a urethane resin which is formed of isocyanate and polyol and therefore possessed of a functional group capable of reacting with the free functional group to be formed on the surface of a coating film in consequence of the discharge treatment mentioned above, the reaction between these functional groups exalts the adhesive strength to a very high extent.

[0017] The coating film on the surface of the profile is only required to be capable of forming such a hydrophilic functional group as mentioned above in consequence of the discharge treatment. As concrete examples of the coating film answering this description, the coating films which result from applying acrylic resin coating material, acryl-melamine resin coating material, polyester coating material, polyurethane coating material, melamine resin coating material, acryl-silicone resin coating material (having two or more fluorine atoms bound to a silane group) by such a coating method as electrodeposition coating, immersion coating, or electrostatic coating may be cited.

[0018] In contrast, as the resin material to be joined to or filled in a profile, various kinds of heat insulating resin such as, for example, urethane resins or epoxy resins of the cold-setting type, or acrylic resins of the photo-setting type can be used. Among other heat insulating resins mentioned above, the urethane resins which possess suitable flexibility at normal room temperatures or in a range of low temperatures and retain strength and suitable rigidity in a range of high temperatures prove to be particularly advantageous.

[0019] As concrete examples of the method for performing the discharge treatment, (1) a method which comprises performing a corona discharge on a given coating film at normal room temperature under normal pressure thereby effecting a surface treatment of the coating film (corona discharge treatment), (2) a method which comprises performing a glow discharge on a given coating film in a vacuum thereby treating the surface of the coating film (ionic treatment), and (3) a method which comprises sealing a given coating film in a vacuum containing a trace quantity of a monomer and an inert gas and performing a glow discharge on the coating film to effect a surface modification of the coating film (plasma treatment) may be cited. These methods are invariably capable of modifying the surface of the coating film of a profile by virtue of electric energy. Among other methods mentioned above, the method of corona discharge treatment which can be carried out rather simply at normal room temperature under normal pressure at a low cost proves to be particularly advantageous. The treating devices available for the corona discharge treatment are broadly known in three types, i.e. a spark gap system, a vacuum tube system, and a solid state system. For the discharge treatment contemplated by the present invention, any of these systems can be effectively adopted.

[0020] The conditions for the discharge treatment are preferred to be set such that the surface of the coating film of a discharge treated profile registers a surface tension of not less than 45 dyn/cm or causes 5  $\mu$ l of a water drop poured thereon to spread over an area of not less than 3.5 mm, preferably not less than 3.7 mm in diameter. These conditions can be adjusted, for example, by suitably setting the speed of conveyance of the profile or the magnitude of discharge voltage or other discharge conditions.

[0021] Now, the present invention will be described more specifically below with reference to the annexed drawings.

[0022] Figs. 1A through 1F illustrate one example of the process to be performed when the method of the present invention is applied to the production of a heat insulating profile.

[0023] First, as illustrated in Fig. 1A, an electrode 20 for discharge treatment is inserted into one (3) of two resin filling recesses 3 and 4 (hereinafter referred to as "pouring pockets") disposed between opposed lateral sheet members 2a and 2b of a coated profile 1 in such a manner as to interconnect the sheet members 2a and 2b and it is operated therein to perform a discharge treatment on the inner surface of the pouring pocket 3. Then, as illustrated in Fig. 1B, a resin 5 is poured into the discharge treated pouring pocket 3 and allowed to set therein. And the profile 1 is turned upside down. By the use of a suitable cutting tool (not shown), part of a bottom portion 4a is cut from the other pouring pocket 4 side as illustrated in Fig. 1C and, at the same time, part of the bottom portion 3a of the other pouring pocket

3 is likewise cut. (Incidentally, when the profile 1 possesses only one pouring pocket 3, the cutting tool may be inserted through an opening on the bottom portion 3a side and manipulated to cut part of the bottom portion 3a.)

[0024] Then, as illustrated in Fig. 1D, a resin sheet 6 is applied fast to the bottom portion 4a of the other pouring pocket 4 so as to cover the cut opening part 4b. Various kinds of synthetic resin sheet may be used as the resin sheet 6. This resin sheet 6 is preferred to be a sheet of polyester which possesses fair rigidity and forms a free hydrophilic functional group like -COOH in consequence of discharge treatment. The thickness of this resin sheet 6 which is proper for the present invention generally falls in the approximate range of 150 - 180  $\mu\text{m}$ , depending on the kind of the resin sheet to be used. Thereafter, as illustrated in Fig. 1E, the electrode 20 for discharge treatment is inserted into the other pouring pocket 4 and operated to perform a discharge treatment on the surfaces of the pouring pocket 4 and resin sheet 6. Subsequently, by pouring the resin 5 into the pouring pocket 4 which has undergone the discharge treatment as described above and allowing the resin to set therein, a heat insulating profile 10 having the opposed lateral sheet members 2a, 2b joined fast integrally to each other with a pair of joined parts formed of the resin 5, as illustrated in Fig. 1F is obtained.

[0025] Alternatively, the process of discharge treatment may be performed first on the upper and lower pouring pockets 3 and 4 (by performing the discharge treatment on the pouring pocket 3 as illustrated in Fig. 1A, then turning the profile 1 upside down, and subsequently performing the discharge treatment on the pouring pocket 4, for example) and thereafter the steps of Figs. 1B, 1C, 1D, and 1F may be carried out.

[0026] In the case of a profile having three pouring pockets, it is manufactured in a structure such that an opening part is formed in advance in the bottom portion of one of the opposite pouring pockets. On this pouring pocket, therefore, the discharge treatment and the filling of resin can be performed in accordance with the process of Figs. 1D through 1F mentioned above.

[0027] Fig. 2 illustrates part of one example of an aluminum sash formed by assembling heat insulating profiles of various structures produced by the method described above. In the diagram, the reference numeral 11 represents an outer meeting stile, 12 a lower rail, 13 a lower frame, and 14 a vertical frame, which are invariably heat insulating structures using the resin 5. The reference numerals 15a and 15b each represent a double-wall glass. Owing to the structure of this sort, the produced aluminum sash excels in the ability to offer insulation from heat, the ability to prevent dew condensation, and the durability. Further, since the component heat insulating profiles excel in adhesive strength with the resin, the aluminum sash will not emit a squeak even when it is accidentally exposed to an external force.

[0028] Fig. 3 is a fragmentary cross section illustrating one example of a heat insulating profile 10a having a hole-forming part 8 for screw protruded into a pouring pocket 7 similarly in the lower rail 12 illustrated in Fig. 2. According to the method of the present invention, the discharge treatment and the filling of resin can be easily performed even on the pouring pocket 7 which is furnished with the hole-forming part 8 for screw.

[0029] Incidentally, a cut part 7b of a bottom portion 7a of the pouring pocket 7 in this structure is generally held to be one of the basal parts of the hole-forming part 8 for screw.

[0030] Fig. 4 illustrates one example of the insertion of a discharge treatment electrode 20a into a pouring pocket 9 of the lower frame 13 illustrated in Fig. 2. The discharge treatment electrode 20a is depicted herein as being lined with a silicone rubber 21.

[0031] The electrode to be used in the discharge treatment can be made in various shapes as illustrated in Fig. 5 through Fig. 9.

[0032] Fig. 5 illustrates an electrode 20b shaped like a round rod and Fig. 6 illustrates an electrode 20c shaped like a plate. These electrodes each have a high-voltage lead wire 23 set in place with a screw in the upper part thereof. The reference numeral 22 represents a porcelain insulator. Fig. 7 illustrates an electrode 20d shaped like a disc. The electrode 20d is rotatably attached to a bracket 25 through the medium of a pin 24 having the high-voltage lead wire 23 connected thereto.

[0033] An electrode 20e illustrated in Fig. 8 has a structure such that a projecting part 27 whose cross section laterally diverges in the shape of the letter V is fixed to the lower terminal portion of a rodlike base part 26 having the high-voltage lead wire 23 connected thereto. The provision of this projecting part 27 brings about such advantages as imparting elasticity to the relevant portion, facilitating the insertion of the electrode into the pouring pocket of the profile in motion on the conveying means, allaying the concentration of discharge on the claws (represented by the reference numeral 29 in Fig. 4, for example) protruding into the pouring pocket, and ensuring easy discharge throughout the entire inner surface of the pouring pocket.

[0034] As the material for the electrode, aluminum, stainless steel, iron, or copper may be used either in a form devoid of a coating or in a form lined with such a dielectric as silicone rubber as illustrated in Fig. 4.

[0035] Fig. 9 illustrates the structure of an electrode which can be used most advantageously for the method of the present invention. This electrode 20f comprises a solid base part 26a shaped like a round rod, a hollow part 26b formed in the lower terminal portion of the base part 26a, and a multiplicity of wires 28 whose upper ends are bundled, inserted in the hollow part 26b, and fixed therein by caulking. Though the lower part of the base part 26a is bent so as to be easily inserted into the pouring pocket of the profile in motion on the conveying means, it may be in a straight shape.

Generally, a standard electrode tends to discharge electricity through the leading end (edge part) thereof during the course of discharge. The present electrode, owing to the incorporation of the bundle of a multiplicity of wires 28 for the sake of discharge, is effective in enlarging the area of discharge, preventing the concentration of discharge on the claws protruding into the pouring pocket, enabling the discharge to occur throughout the entire inner surface (bottom surface and lateral surfaces) of the pouring pocket, and ensuring improvement of the surface modification of the coating film forming the inner surface of the pouring pocket. The unit diameter of the wires 28, the quantity thereof, and the positions of their leading terminals can be suitably adjusted in accordance with the cross-sectional shape, size, etc. of the recess (pouring pocket) subjected to the discharge treatment. In the case of the standard heat insulating profile, it is desirable that the unit diameter of the wires be not more than 1 mm, preferably in the range of 0.1 - 0.7 mm, and the quantity thereof be not more than 100. Optionally, the component wire may be formed by intertwining still thinner wires. In this case, since the leading terminal parts of the wires come apart and expose the leading terminal parts of a greater number of thinner wires, they allow easy discharge of electricity. Since the component wires are further endowed with elasticity, they are at an advantage in resuming their original shape perfectly after the discharge treatment which is performed while they are sliding in a bent form on the inner surface of the pouring pocket.

**[0036]** Fig. 10 schematically illustrates the state in which a corona discharge treatment is performed on the profile 1 which is in motion on a conveying device 40 of the conveyor roller type.

**[0037]** The electrode 20 is fitted to an elevating plate 30 through the medium of the porcelain insulator 22 and the periphery of the electrode 20 is enclosed with an electrode cover 31 made of synthetic resin and fitted to the elevating plate 30. The reference numeral 32 represents an electrode gap adjuster for adjusting the distance between the leading terminal of the electrode 20 and the profile 1. The conveying device 40 is provided in the part thereof falling directly below the electrode 20 with a metallic drive roller 41, which is connected to the grounding side of a high-frequency oscillator 33. The electrode 20 is connected to a high-voltage transformer 34 through the medium of the high-voltage lead wire 23. When the corona discharge is generated by the application of a high voltage between the electrode 20 inserted in the pouring pocket 1a of the profile 1 and the profile 1 held in contact with the metallic drive roller 41, therefore, the corona discharge treatment is continuously performed on the inner surface of the pouring pocket 1a of the profile 1 which is in motion on the conveying device 40. The other drive rollers 42 used in the conveying device 40 are rollers lined with rubber. Though the speed of conveyance of the profile is suitably adjusted, it is preferred to be in the approximate range of 5 - 60 m/min. The high-frequency power source for the corona discharge has a frequency generally in the range of 8,000 - 35,000 Hz, preferably below 10,000 Hz, and a voltage of not less than 0.5 kV, preferably not less than 3 kV.

**[0038]** Incidentally, the corona discharge treatment is effected at a high frequency and a high voltage. The high-voltage part, when approached by a human body, has the possibility of emitting a spark and burning the skin of the human body. For preventing this accident, the electrode 20 and the metallic drive roller 41 are encircled with a protective frame, which is omitted from illustration here by reason of a limited space. When the corona discharge is effected in the air, it emits  $O_3$  and  $NO_x$ , which have adverse effects on the health of the operator. The room in which the treatment is performed, therefore, must be furnished with a duct extended to the exterior of the room so that the air therein may remain clean at all times. Alternatively, the protective frame mentioned above may be substituted by a protective box which is adapted to ventilate the room interior.

**[0039]** Fig. 11 schematically illustrates the structure of an electrode position adjusting device 50. The electrode position adjusting device 50 is furnished with a pair of laterally disposed supporting bases 51a and 51b, a sliding table 55 slidably mounted on the supporting bases 51a and 51b, and a framework 60 as a supporting member raised erect from the rear edge part of the sliding table 55.

**[0040]** On the upper sides of the supporting bases 51a and 51b, rails 52a and 52b are disposed perpendicularly to the conveying device mentioned above and parallel to the metallic drive roller 41 as centered therearound. On one lateral part of the supporting base 51b, a threaded rod 53 fitted with a handle 54 is rotatably disposed as shown in Fig. 11. On one lateral part of the sliding table 55, a female screw member 56 of ball thread adapted to mesh with the threaded rod 53 mentioned above is fixedly secured. In the central part of the lower side of the sliding table 55, a rotary shaft 57 is rotatably disposed parallel to the rails 52a and 52b. To the leading terminal of the rotary shaft 57, a handle 58 is fitted. To the rear terminal thereof, a bevel gear 59 is fitted. In the central part of the framework 60 raised upright from the rear edge part of the sliding table 55, a threaded rod 61 for vertically moving the elevating plate is disposed in a vertical direction. To the lower terminal of the threaded rod 61, a bevel gear 62 adapted to mesh with the bevel gear 59 of the rotary shaft 57 mentioned above is fitted. On the front sides of the opposite frames of the framework 60, a pair of laterally opposite guide bars 63a and 63b are disposed in the vertical direction as separated by a prescribed distance. Stoppers 64a and 64b are fitted to the predetermined position of the guide bars 63a and 63b. On the rear side of the vertical part 30a of the elevating plate 30 having the electrode (the electrode 20f illustrated in Fig. 9 in the structure illustrated in Fig. 11) fitted thereto through the medium of the porcelain insulator 22, a female screw member 65 is disposed on the center thereof and a pair of guide members 66a and 66b are disposed on either lateral sides thereof, each projected rearward. The female screw member 65 is meshed with the threaded rod 61. The guide bars

63a and 63b mentioned above are inserted through the vertical through holes of the guide members 66a and 66b.

[0041] Now, the operation of the electrode position adjusting device 50 will be explained below. First, when the threaded rod 53 is rotated with the handle 54, the sliding table 55 is slid forward and backward on the rails 52a and 52b of the supporting bases 51a and 51b through the medium of the female screw member 56 which is meshed with the threaded rod 53. The sliding table 55 is adapted to assume its vertical position at a predetermined distance below from the driving rollers 41 and 42 of the conveying device 40 illustrated in Fig. 10. After the sliding table 55 has been advanced until the electrode 20f is positioned on the profile conveying path of the conveying device 40, the rotary shaft 57 is rotated with the handle 58. As a result, the threaded rod 61 is rotated through the medium of the bevel gear 62 meshed with the bevel gear 59 at the rear terminal of the rotary shaft 57. In consequence of this rotation of the threaded rod 61, the elevating plate 30 is made to produce a vertical motion through the medium of the female screw member 65 which is meshed with the threaded rod 61. The fall of the elevating plate 30 is stopped when the lower terminal of the vertical part 30a thereof collides against the stopper 64a and 64b and is no longer allowed to continue. Thus, the lowermost position of the electrode 20f is fixed by the stoppers 64a and 64b. In order for the lowermost position to be adjusted when the electrode is replaced, the stoppers 64a and 64b may be fitted vertically adjustably to the guide bars 63a and 63b.

[0042] After the position of the electrode 20f on the conveying device 40 has been adjusted as described above, the profile 1 is conveyed on the conveying device 40 as illustrated in Fig. 10 and the pouring pocket 1a thereof is meanwhile subjected to the discharge treatment.

[0043] Optionally, the guide bars 63a and 63b formed in a prescribed length may be fixed to the vertical part 30a of the elevating plate 30 and these guide bars may be fitted vertically movably to the framework 60 and adapted such that the fall of the elevating plate 30 may stop when the lower terminals of the guide bars collide against the upper sides of the sliding table 55. For the purpose of allowing automatic adjustment of the positions of the electrode 20f in the forward and the backward direction when the profile 1 being conveyed on the conveying device 40 deviates from the path of conveyance, a profile position sensor may be disposed at a prescribed position of the conveying device 40 and an AC servo motor, for example, may rotate the threaded rod 53 in response to a signal from the sensor so as to set the electrode 20f in the right position.

[0044] Fig. 12 and Fig. 13 illustrate the state in which the discharge treatment is performed on the profile 1 in conveyance, respectively with the electrode 20c shaped like a plate as illustrated in Fig. 6 and the electrode 20d shaped like a disc as illustrated in Fig. 7 inserted into the pouring pocket 1a of the profile 1.

[0045] The pouring pocket 1a of the profile 1 which has undergone the discharge treatment as described above is then filled with resin as illustrated in Fig. 14.

[0046] Fig. 14 illustrates one example of the injection of urethane resin. Isocyanate and polyol which have been pneumatically conveyed in a volumetric ratio of 1 : 1 from the respective storage tanks (not shown) are fed into a mixing chamber 70 and stirred therein with a mixing rotor 71. The resultant mixture is continuously injected via an injection pipe 72 into the pouring pocket 1a of the profile 1 being conveyed on the conveying device (Fig. 10). After the resin injection operation, the mixing chamber 70 has the interior thereof cleaned with a solvent. Though the conditions for the injection of the resin may be suitably set depending on such factors as the inner volume of the pouring pocket, it is generally advantageous to fix the conveying speed of the profile in the approximate range of 10 - 30 m/min., the rotating speed of the mixing rotor 71 in the approximate range of 3,000 - 5,000 revolutions per min., and the amount of the urethane resin to be released in the approximate range of 1 - 5 liters/min. The position of the injection pipe 72 may be adjusted essentially in the same way as described above in respect to the adjustment of the position of electrode.

[0047] After the urethane resin which has been injected is set, part of the bottom portion 1b of the pouring pocket 1a is cut. This practice is the same as in the production of the conventional heat insulating profile, it will be omitted from the description given below.

[0048] Then, the heat insulating profile manufactured in accordance with the present invention will be described below with reference to specific data.

[0049] The samples manufactured herein were extruded profiles of aluminum electrophoretically coated with three kinds of acrylic coating material, with the pouring pockets thereof subjected to a corona discharge treatment and then filled with urethane resin.

[0050] Fig. 15 through Fig. 17 show changes of the amount of functional groups in the surface of a coating film before and after the discharge treatment; Fig. 15 representing the data obtained of a matt coating material, Fig. 16 the data of a white matt coating material, and Fig. 17 the data of a luster coating material. As clearly noted from the analytical results shown in Fig. 15 through Fig. 17 that the discharge treatment resulted in a conspicuous increase of the -COOH group. This marked improvement may be logically explained by a supposition that the discharge treatment resulted in cutting the ester bonds of the acrylic resin. The changes of the amount of functional groups (vertical axis) shown in Fig. 15 through Fig. 17 were obtained by causing a reaction reagent, i.e. silver nitrate with respect to -COOH, p-chlorophenyl isocyanate with respect to -OH, or p-chlorophenyl hydrazine with respect to -C = O, to react with the surface of a given coating film, then analyzing the reagent fixed on the surface of the coating film with ESCA (electron

spectroscopy for chemical analysis) to determine the ESCA-sensitive element (silver, chlorine) of the reagent, and displaying the magnitudes of relative intensity of the peaks (ESCA output) in the curves. While the reagent is fixed on the surface of the coating film when a functional group capable of reacting with the reagent is present in the surface of the coating film, the reagent is easily washed out with a solvent in the absence of such a functional group.

5 [0051] Before and after the discharge treatment, 5  $\mu$ l of a water drop were poured on the surface of a given coating film and the surface was examined to determine the area (diameter) of the surface covered with the spread film of water. The results are shown in the following table.

Table

Kind of coating film	Spread of wet with water drops (diameter, mm)	
	No discharge treatment made	Discharge treatment made
Matt coating material	2.8	3.7 - 3.8
Luster coating material	2.9	3.9
White matt coating material	2.7 - 2.8	3.7 - 3.8

[0052] It is clearly noted from the table given above that on all the coating films, the discharge treatment widened the area of spread of water, added to the wettability (hydrophilicity) of the coating film, or exalted the surface tension.

20 [0053] Then, from the manufactured heat insulating profiles, test pieces (50 X 43 mm = 2150 mm<sup>2</sup>, urethane resin thickness about 6 mm, layer composition: electrophoretically coated aluminum sheet/urethane resin/electrophoretically coated aluminum sheet) were cut and subjected to a tensile test. The test was performed after the urethane resin poured in the profile was left curing for 24 hours. In the test, the tension was applied perpendicularly to the surface of the test piece at a rate of 1 mm/min. As a result, the maximum tensile strength, 311.3 kgf (matt coating material), 363.7 kgf (luster coating material), and 449.2 kgf (white matt coating material) (invariably the average value of three measurements), was obtained.

25 [0054] In a separate test for shear strength which was carried out by keeping one of the electrophoretically coated aluminum sheet fixed and applying a load to the other electrophoretically coated aluminum sheet under the condition of shear rate of 1mm/min., the maximum shear strength, 305.7 kgf (matt coating material), 594.5 kgf (luster coating material), and 477.8 kgf (white matt coating material) (invariably the average of three measurements), was obtained.

30 [0055] It is noted from the test results mentioned above that the discharge treatment fairly added to the adhesive strength of the profile and the resin.

[0056] Then, heat insulating profiles designed for left vertical frame, right vertical frame, upper frame, and lower frame were manufactured in the same manner as described above, with or without a discharge treatment. They were retained at 60°C for 16 hours, at 23 °C for one hour, then at -20°C for six hours, and thereafter at 23°C for one hour, and subsequently they were returned to the first retention at 60 °C for 16 hours. This cycle of heat treatment was repeated by way of a cooling-heating repeating test. The results are shown in Fig. 18.

40 [0057] It is clearly noted from Fig. 18 that the discharge treatment prevented the packed urethane resin from shrinking after the cooling-heating repeating test mentioned above. The profiles for the left vertical frame, right vertical frame, upper frame, and lower frame which had undergone the discharge treatment registered identical results. Fig. 18, therefore, shows one representative data.

45 [0058] While certain specific embodiments have been disclosed herein, the invention may be embodied in other specific forms without departing from the spirit or essential characteristics thereof. The described embodiments are therefore to be considered in all respects as illustrative and not restrictive, the scope of the invention being indicated by the appended claims rather than by the foregoing description and all changes which come within the meaning and range of equivalency of the claims are, therefore, intended to be embraced therein.

## Claims

- 50 1. A method for the production of a resin-composite aluminum profile, **characterized by** comprising the steps of:
- providing an aluminum profile having a coating film applied thereon,  
performing a discharge treatment on the coated surface of a portion of said profile destined for union with resin, and  
55 joining a resin material to said discharge treated portion, **characterized in that** said coating film is formed from a synthetic acrylic resin coating material capable of forming a free hydrophilic functional group in conse-



quence of said discharge treatment, wherein the synthetic acrylic resin forming the coating film contains ester bonds which are cut by the discharge treatment.

2. The method according to claim 1, wherein said aluminum profile has at least one recess intended to be filled with resin, said discharge treatment is performed on the coated inner surface of said recess, and said resin material is filled in said discharge treated recess.
3. A method according to claim 1, wherein said aluminum profile having a coating film applied thereon comprises opposed lateral sheet members and a recess disposed between said members and intended to be filled with resin, and said discharge treatment is performed on the coated inner surface of the recess of said profile, said method further comprising the steps of:
  - filling a resin material in said discharge treated recess, and
  - cutting a portion of the aluminum profile forming said recess thereby obtaining a heat insulating profile having the opposed lateral sheet members integrally joined to each other with said resin material.
4. The method according to claim 3, wherein said aluminum profile has at least two recesses disposed between opposed lateral sheet members and adapted to be filled with resin, the discharge treatment and the filling with the resin material are performed in one of said recesses, then the portion of the aluminum profile forming the other recess is cut at the time that the portion of the aluminum profile forming said one recess is cut, a resin sheet is superposed on the cut portion of said other recess to occlude said cut portion, and subsequently the discharge treatment and the filling with resin are performed inside said other recess.
5. The method according to any of claims 1 to 4, wherein said coating film is formed on said aluminum profile by at least one method selected from the group consisting of electrodeposition coating, immersion coating, and electrostatic coating.
6. The method according to any of claims 1 to 5, wherein said resin material for filling is a urethane resin substantially formed of isocyanate and polyol and said aluminum profile has a coating film formed from a coating material capable of forming a functional group, which reacts with isocyanate, in consequence of said discharge treatment.
7. The method according to any of claims 1 to 6, wherein the coated surface of said aluminum profile is discharge treated until the surface energy thereof reaches a level of not less than 45 dyn/cm or the spread of a 5  $\mu$ l water drop poured thereon reaches a diameter of not less than 3.5 mm.
8. The method according to any of claims 1 to 7, wherein said discharge treatment is corona discharge treatment.
9. The method according to any of claims 4 to 8, wherein said resin sheet is made of polyester.
10. A resin-composite aluminum profile comprising:
  - an aluminum profile having a coating film applied thereon, at least part of the coated surface of said profile being discharge treated, and
  - a resin material joined to the discharge treated part of said aluminum profile, **characterized in that** said profile is obtainable by the method according to claim 1.
11. The profile according to claim 10, wherein said aluminum profile comprises opposed lateral sheet members having a coating film applied thereon, said lateral sheet members each having a discharge treated part in the opposed, coated surface thereof, and
  - a joining member connecting said lateral sheet member, said joining member being formed on a resin material integrally joined between the discharge treated parts of the opposed surfaces of said opposed lateral sheet members.
12. The profile according to claim 11, wherein said aluminum profile has at least a pair of discharge treated, opposed recesses respectively formed in the opposed surface of said lateral sheet members and said joining member is joined to said recesses.

13. The profile according to any of claims 10 to 12, wherein said resin material is a urethane resin substantially formed of isocyanate and polyol and said aluminum profile has a coating film formed from a coating material capable of forming a functional group, which reacts with isocyanate, in consequence of a discharge treatment.

5

## Patentansprüche

1. Verfahren für die Herstellung eines Aluminium-Harz-Verbundprofils, **gekennzeichnet durch** folgende Schritte:

10

Bereitstellen eines Aluminiumprofils mit einem darauf aufgetragenen Beschichtungsbelag,

Ausführen einer Entspannungsbehandlung auf der beschichteten Fläche eines Abschnitts des Profils, der für die Verbindung mit dem Harz bestimmt ist, und

15

Verbinden eines Harzwerkstoffs mit dem entspannungsbehandelten Abschnitt, **dadurch gekennzeichnet, dass** der Beschichtungsbelag aus synthetischem Acrylharzwerkstoff ausgebildet ist, der geeignet ist, infolge der Entspannungsbehandlung eine freie hydrophile Funktionsgruppe auszubilden, wobei das synthetische Acrylharz, das den Beschichtungsbelag ausbildet, Esterbindungen enthält, die **durch** die Entspannungsbehandlung gespalten werden.

20

2. Verfahren nach Anspruch 1, wobei das Aluminiumprofil mit mindestens einer Vertiefung ausgestattet ist, die mit Harz gefüllt werden soll, die Entspannungsbehandlung an der beschichteten Innenfläche der Vertiefung ausgeführt wird und der Harzwerkstoff in die entspannungsbehandelte Vertiefung gefüllt wird.

25

3. Verfahren nach Anspruch 1, wobei das Aluminiumprofil das mit einem darauf aufgetragenen Beschichtungsbelag ausgestattet ist, gegenüberliegende seitliche Plattenelemente und eine Vertiefung umfasst, die zwischen den Elementen angeordnet ist und mit Harz gefüllt werden soll, und die Entspannungsbehandlung an der beschichteten Innenfläche der Vertiefung des Profils ausgeführt wird, wobei das Verfahren die folgenden Schritte umfasst:

30

Füllen eines Harzwerkstoffs in die entspannungsbehandelte Vertiefung und

Schneiden eines Abschnitts des Aluminiumprofils, das die Vertiefung ausbildet, um dadurch ein wärmeisolierendes Profil zu erhalten, das mit gegenüberliegenden seitlichen Plattenelementen ausgestattet ist, die einstückig miteinander mit dem Harzwerkstoff verbunden sind.

35

4. Verfahren nach Anspruch 3, wobei das Aluminiumprofil mit mindestens zwei Vertiefungen ausgestattet ist, die zwischen gegenüberliegenden seitlichen Plattenelementen angeordnet sind und geeignet sind, mit Harz befüllt zu werden, die Entspannungsbehandlung und das Füllen mit dem Harzwerkstoff in einer der Vertiefungen ausgeführt werden, dann der Abschnitt des Aluminiumprofils, der die andere Vertiefung bildet, geschnitten wird, wenn der Abschnitt des Aluminiumprofils, der die eine Vertiefung bildet, geschnitten wird, eine Harzplatte über den geschnittenen Abschnitt der anderen Vertiefung gelegt wird, um den abgeschnittenen Abschnitt abzudecken, und nachfolgend die Entspannungsbehandlung und das Füllen mit Harz innerhalb der anderen Vertiefung ausgeführt werden.

40

45

5. Verfahren nach einem der Ansprüche 1 bis 4, wobei der Beschichtungsbelag durch mindestens eines der Verfahren wie Galvanisieren, Tauchlackierung und elektrostatische Beschichtung auf das Aluminiumprofil aufgebracht wird.

50

6. Verfahren nach einem der Ansprüche 1 bis 5, wobei das Harzmaterial zum Füllen ein Urethanharz ist, das im Wesentlichen aus Isocyanat und Polyol gebildet ist, und das Aluminiumprofil mit einem Beschichtungsbelag ausgestattet ist, der aus einem Beschichtungsmaterial gebildet wird, das geeignet ist, eine Funktionsgruppe auszubilden, die mit Isocyanat infolge der Entspannungsbehandlung reagiert.

55

7. Verfahren nach einem der Ansprüche 1 bis 6, wobei die beschichtete Oberfläche des Aluminiumprofils entspannungsbehandelt wird, bis ihre Oberflächenenergie einen Bereich von mindestens 45 dyn/cm erreicht oder die Ausbreitung eines 5 µl großen Wassertropfens, der darauf gegossen wird, einen Durchmesser von mindestens 3,5 mm erreicht.

8. Verfahren nach einem der Ansprüche 1 bis 7, wobei die Entspannungsbehandlung eine Corona-Entspannungs-

behandlung ist.

9. Verfahren gemäß einem der Ansprüche 4 bis 8, wobei die Harzplatte aus Polyester hergestellt ist.

5 10. Aluminium-Harz-Verbundprofil umfassend:

ein Aluminiumprofil, das mit einem Beschichtungsbelag ausgestattet ist, der darauf aufgebracht ist, wobei mindestens ein Teil der beschichteten Oberfläche des Profils entspannungsbehandelt ist, und

10 einen Harzwerkstoff, der mit dem entspannungsbehandelten Teil des Aluminiumprofils verbunden ist, **dadurch gekennzeichnet, dass** das Profil durch das Verfahren nach Anspruch 1 erhalten werden kann.

11. Profil nach Anspruch 10, wobei das Aluminiumprofil Folgendes umfasst:

15 gegenüberliegende seitliche Plattenelemente, die mit einem darauf aufgetragenen Beschichtungsbelag ausgestattet sind, wobei die seitlichen Plattenelemente jeweils mit einem entspannungsbehandelten Teil in deren gegenüberliegender, beschichteter Oberfläche ausgestattet sind, und

20 ein Verbindungselement, das das seitliche Plattenelement verbindet, wobei das Verbindungselement an einem Harzwerkstoff ausgebildet ist, der einstückig zwischen den entspannungsbehandelten Teilen der gegenüberliegenden Flächen der gegenüberliegenden seitlichen Plattenelemente verbunden ist.

25 12. Profil nach Anspruch 11, wobei das Aluminiumprofil mit mindestens einem Paar entspannungsbehandelter, gegenüberliegender Vertiefungen ausgestattet ist, die jeweils in der gegenüberliegenden Oberfläche der seitlichen Plattenelemente ausgebildet sind und das Verbindungselement mit den Vertiefungen verbunden ist.

30 13. Profile nach einem der Ansprüche 10 bis 12, wobei der Harzwerkstoff ein Urethanharz ist, das im Wesentlichen aus Isocyanat und Polyol gebildet ist, und das Aluminiumprofil mit einem Beschichtungsbelag ausgestattet ist, der aus einem Beschichtungsmaterial ausgebildet ist, das eine Funktionsgruppe bilden kann, die aufgrund einer Entspannungsbehandlung mit Isocyanat reagieren kann.

## Revendications

35 1. Procédé de production d'un profilé mixte résine-aluminium, **caractérisé en ce qu'il** comprend les étapes consistant à :

proposer un profilé aluminium ayant un film de revêtement appliqué sur celui-ci ;

40 réaliser un traitement par décharge sur la surface recouverte d'une partie dudit profilé destiné à être lié à la résine, et

45 ajouter un matériau résineux à ladite partie traitée par décharge, **caractérisé en ce que** le film de revêtement est formé à partir d'un produit de revêtement à base de résine acrylique synthétique capable de former un groupe fonctionnel hydrophile libre suite audit traitement par décharge, dans lequel la résine acrylique synthétique formant le film de revêtement comprend des liaisons ester qui sont coupées par le traitement par décharge.

50 2. Procédé selon la revendication 1, dans lequel ledit profilé aluminium présente au moins une cavité destinée à être remplie de résine, ledit traitement par décharge est réalisé sur la surface interne recouverte de ladite cavité, et ledit matériau résineux est versé dans ladite cavité traitée par décharge.

55 3. Procédé selon la revendication 1, dans lequel ledit profilé aluminium ayant un film de revêtement appliqué sur celui-ci comprend des pièces en tôle latérale opposées et une cavité située entre lesdites pièces et destinées à être remplies de résine, et ledit traitement par décharge est effectué sur la surface interne recouverte de la cavité dudit profilé, ledit procédé comprenant également les étapes consistant à :

verser un matériau résineux dans ladite cavité traitée par décharge, et

couper une partie du profilé aluminium formant ladite cavité, en obtenant ainsi un profilé isolant ayant les pièces en tôle latérale opposées complètement collées l'une à l'autre avec ledit matériau résineux.

- 5        4. Procédé selon la revendication 3, dans lequel ledit profilé aluminium présente au moins deux cavités disposées entre les pièces en tôle latérale opposées et adaptées pour être remplies de résine, le traitement par décharge et le remplissage avec le matériau résineux sont effectués dans une desdites cavités, puis la partie du profilé aluminium formant l'autre cavité est coupée au moment où la partie du profilé aluminium formant une desdites cavités est coupée, une feuille de résine est superposée sur la partie coupée de ladite autre cavité pour occlure ladite partie coupée, puis le traitement par décharge et le remplissage avec la résine sont effectués à l'intérieur de ladite  
10        autre cavité.
- 15        5. Procédé selon l'une quelconque des revendications 1 à 4, dans lequel ledit film de revêtement est formé sur ledit profilé aluminium à l'aide d'au moins un procédé choisi parmi le groupe comprenant le revêtement par dépôt électrolytique, le revêtement par immersion et le revêtement électrostatique.
- 20        6. Procédé selon l'une quelconque des revendications 1 à 5, dans lequel le matériau résineux de remplissage est une résine uréthane essentiellement constituée d'isocyanate et de polyol et ledit profilé aluminium présente un film de revêtement formé à partir d'un matériau de revêtement capable de former un groupe fonctionnel, qui réagit avec l'isocyanate, suite au dit traitement par décharge.
- 25        7. Procédé selon l'une quelconque des revendications 1 à 6, dans lequel la surface recouverte dudit profilé aluminium est traitée par décharge jusqu'à ce que l'énergie de surface de celle-ci atteigne un niveau supérieur à 45 dynes/cm ou que la dispersion d'une goutte d'eau de 5 µl versée sur celle-ci atteigne un diamètre supérieur à 3,5 mm.
- 30        8. Procédé selon l'une quelconque des revendications 1 à 7, dans lequel ledit traitement par décharge est un traitement par décharge corona.
- 35        9. Procédé selon l'une quelconque des revendications 4 à 8, dans lequel ladite feuille de résine est constituée de polyester.
- 40        10. Profilé mixte résine-aluminium comprenant :  
un profilé aluminium ayant un film de revêtement appliqué sur celui-ci, au moins une partie de la surface recouverte dudit profilé étant traitée par décharge, et  
un matériau résineux ajouté à la partie traitée par décharge dudit profilé aluminium, **caractérisé en ce que** ledit profilé peut être obtenu à l'aide du procédé selon la revendication 1.
- 45        11. Profilé selon la revendication 10, dans lequel ledit profilé aluminium comprend des pièces en tôle latérale opposées ayant un film de revêtement appliqué sur celles-ci, lesdites pièces en tôle latérale ayant chacune une partie traitée par décharge dans la surface recouverte opposée de celle-ci, et une pièce de fixation raccordant ladite pièce en tôle latérale, ladite pièce de liaison étant formée sur un matériau résineux intégralement fixé entre les parties traitées par décharge des surfaces opposées desdites pièces en tôle latérale opposées.
- 50        12. Profilé selon la revendication 11, dans lequel ledit profilé aluminium présente au moins une paire de cavités opposées traitées par décharge respectivement formées dans la surface opposée desdites pièces en tôle latérale et ladite pièce de fixation est fixée auxdites cavités.
- 55        13. Profilé selon l'une quelconque des revendications 10 à 12, dans lequel ledit matériau résineux est une résine uréthane essentiellement constituée d'isocyanate et de polyol et ledit profilé présente un film de revêtement formé à partir d'un matériau de revêtement capable de former un groupe fonctionnel, qui réagit avec l'isocyanate, suite à un traitement par décharge.

FIG. 1A

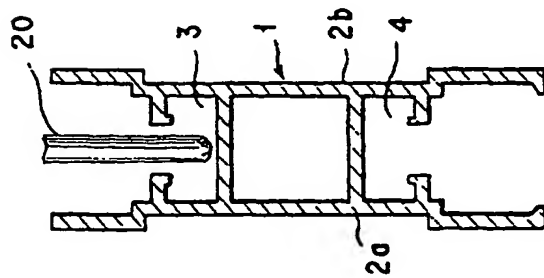


FIG. 1B

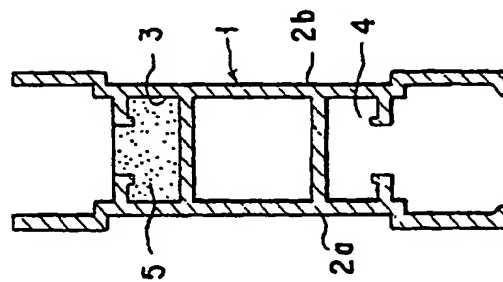


FIG. 1C

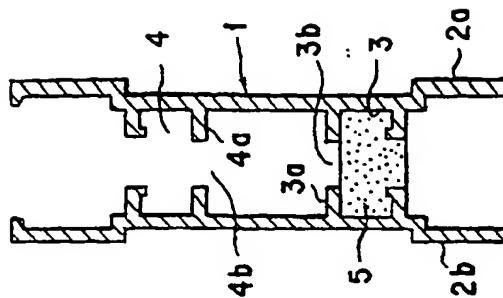


FIG. 1F

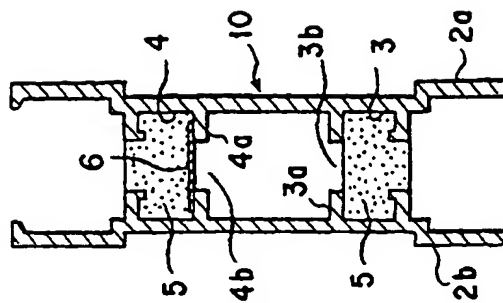


FIG. 1E

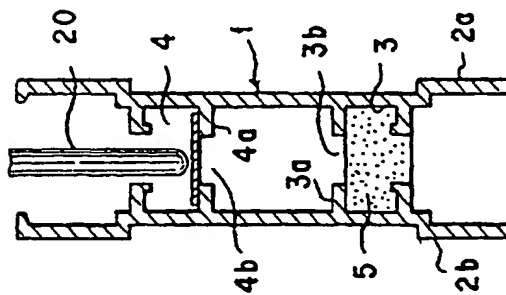
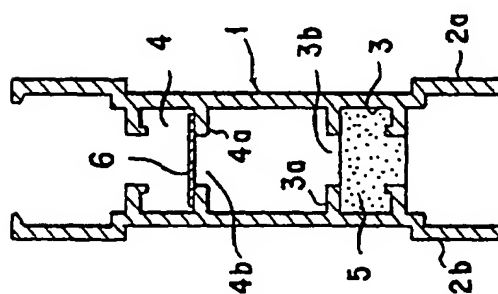


FIG. 1D



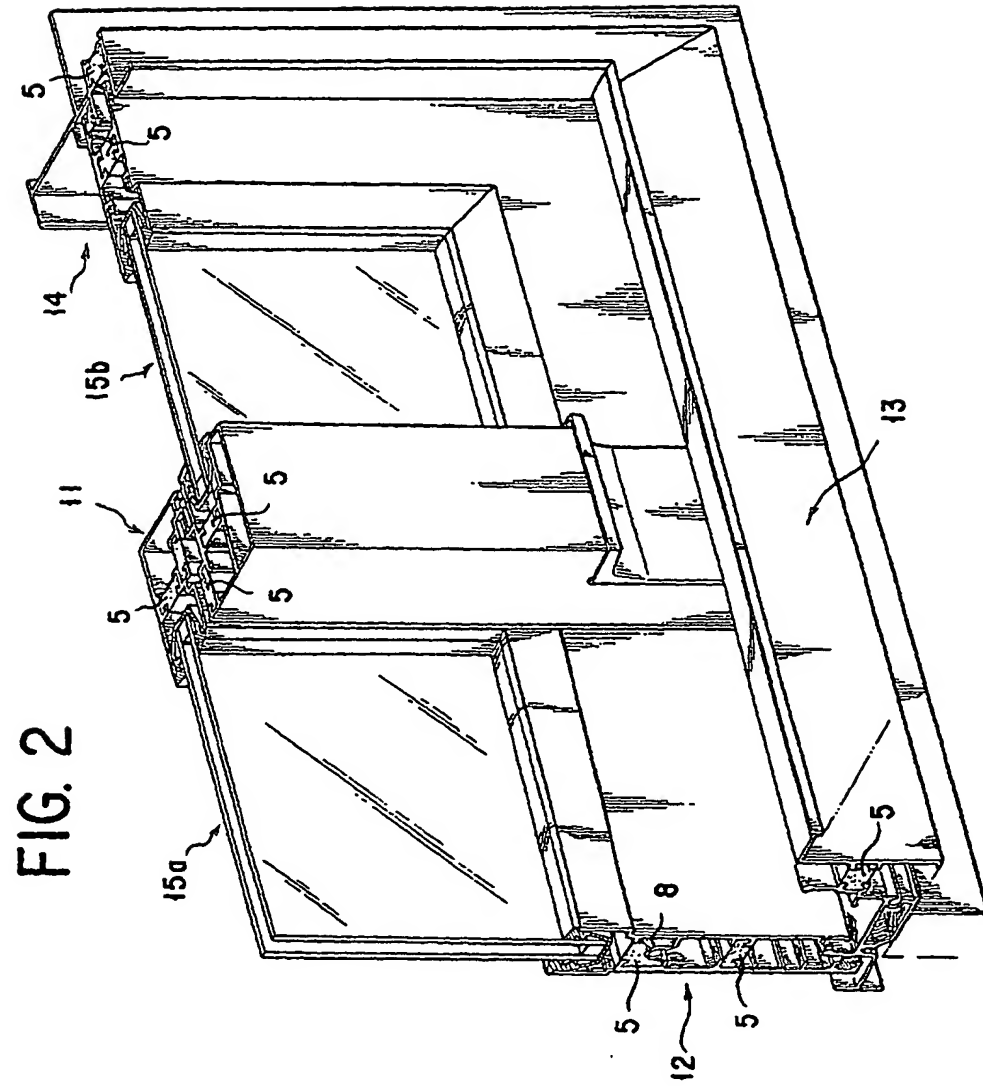


FIG. 3

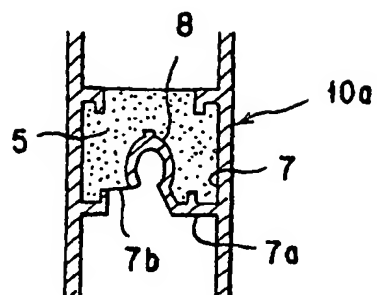


FIG. 4

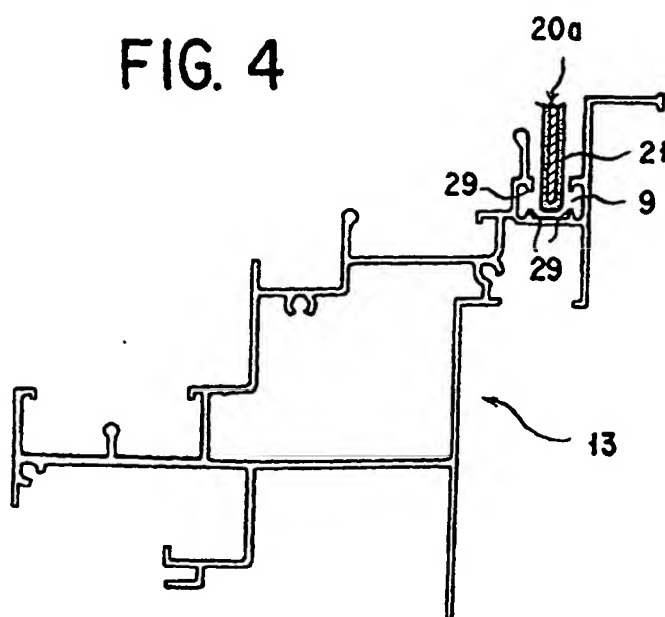




FIG. 5

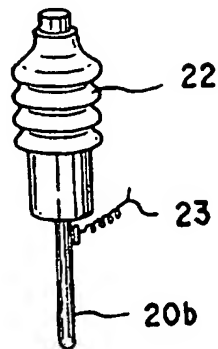


FIG. 6

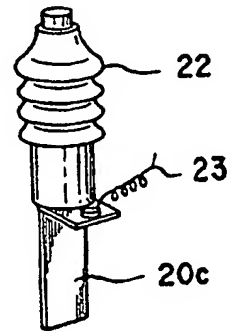


FIG. 7

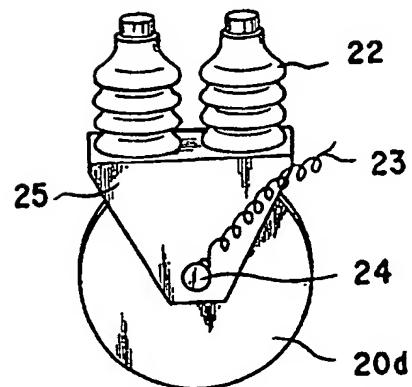


FIG. 8

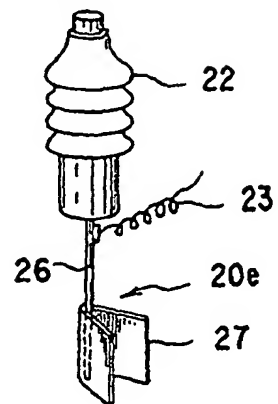
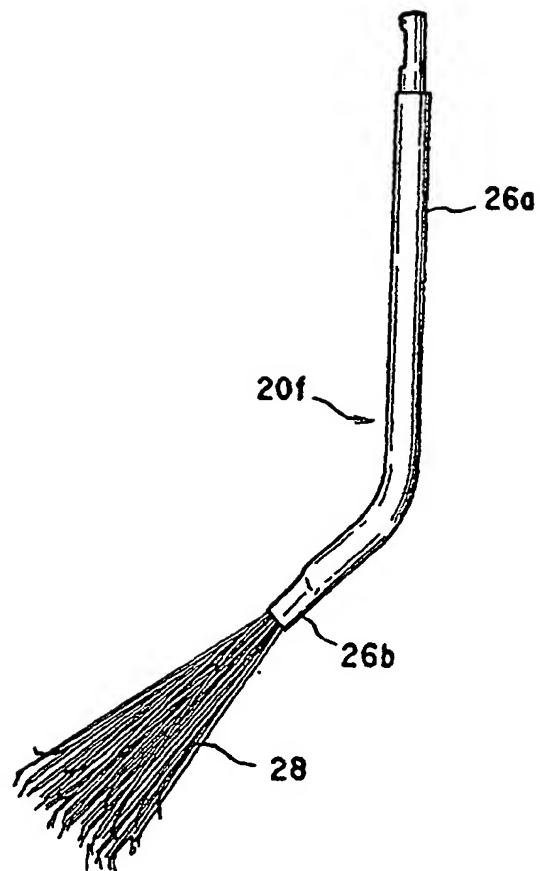


FIG. 9



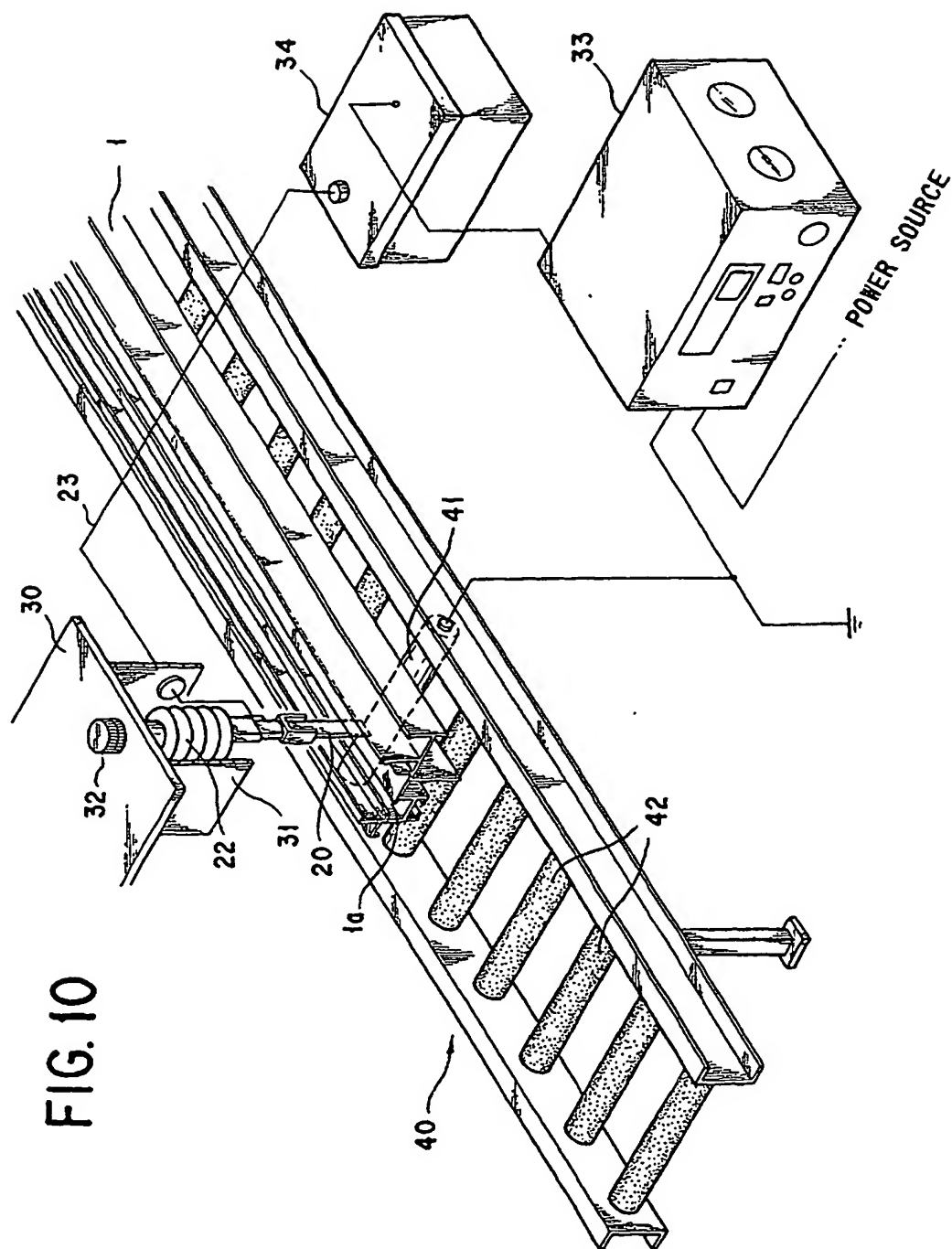


FIG. 10

FIG. 11

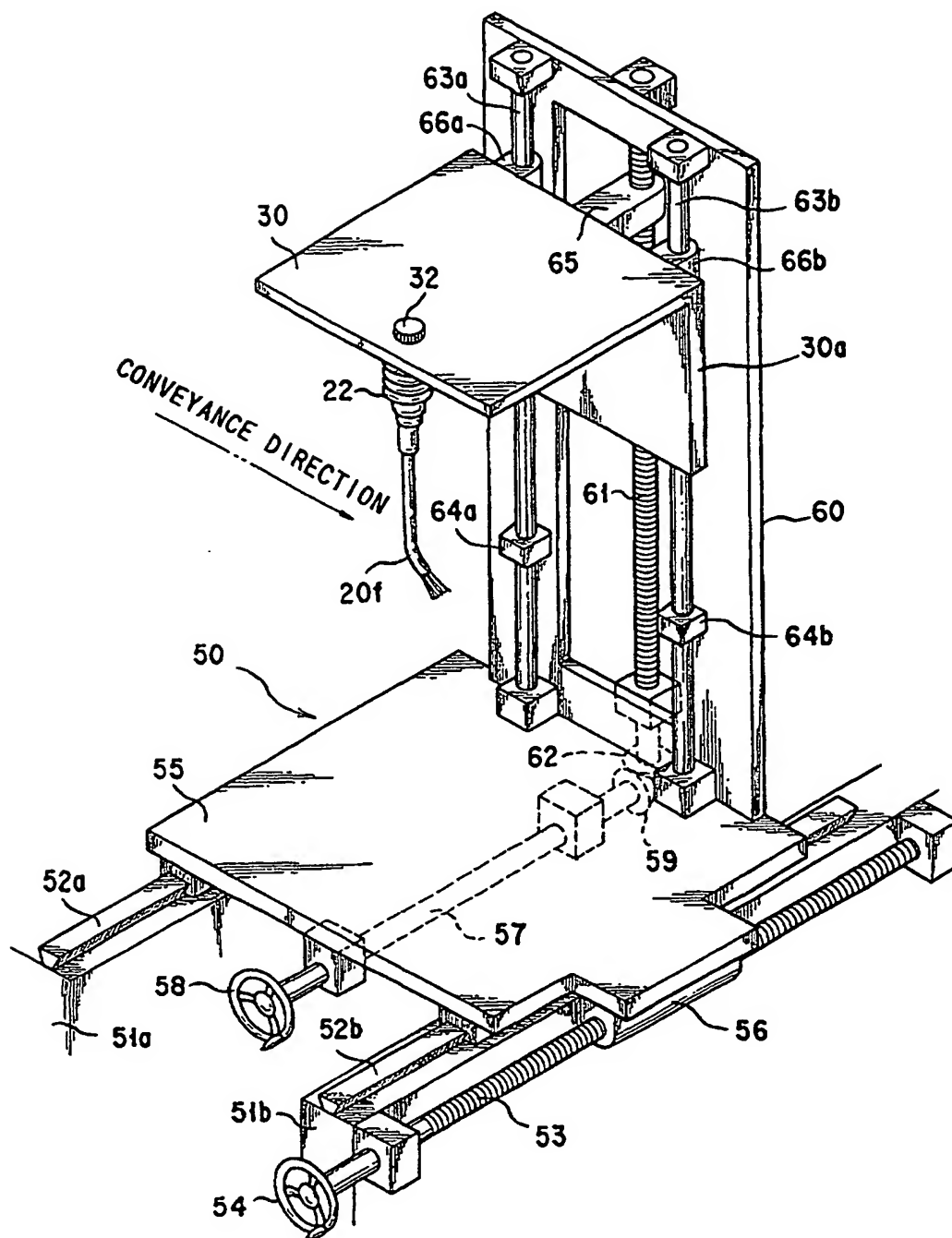


FIG. 12

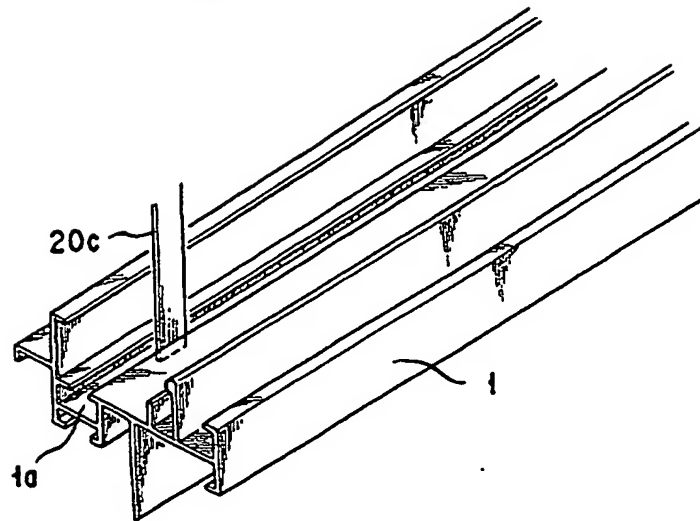


FIG. 13

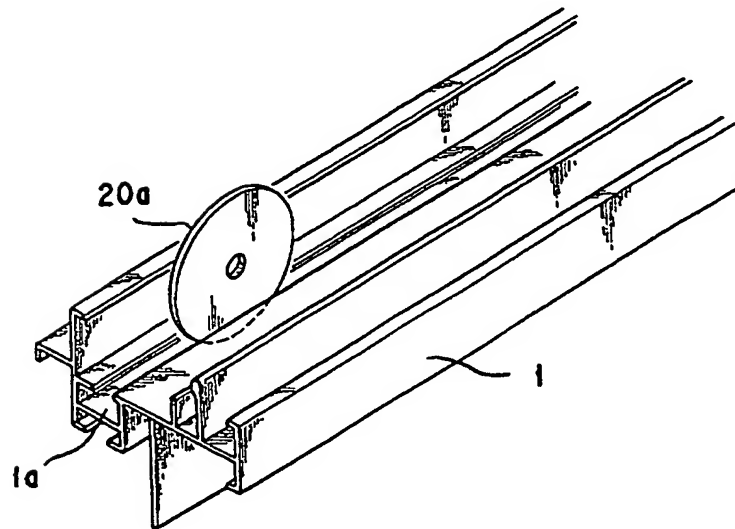


FIG. 14

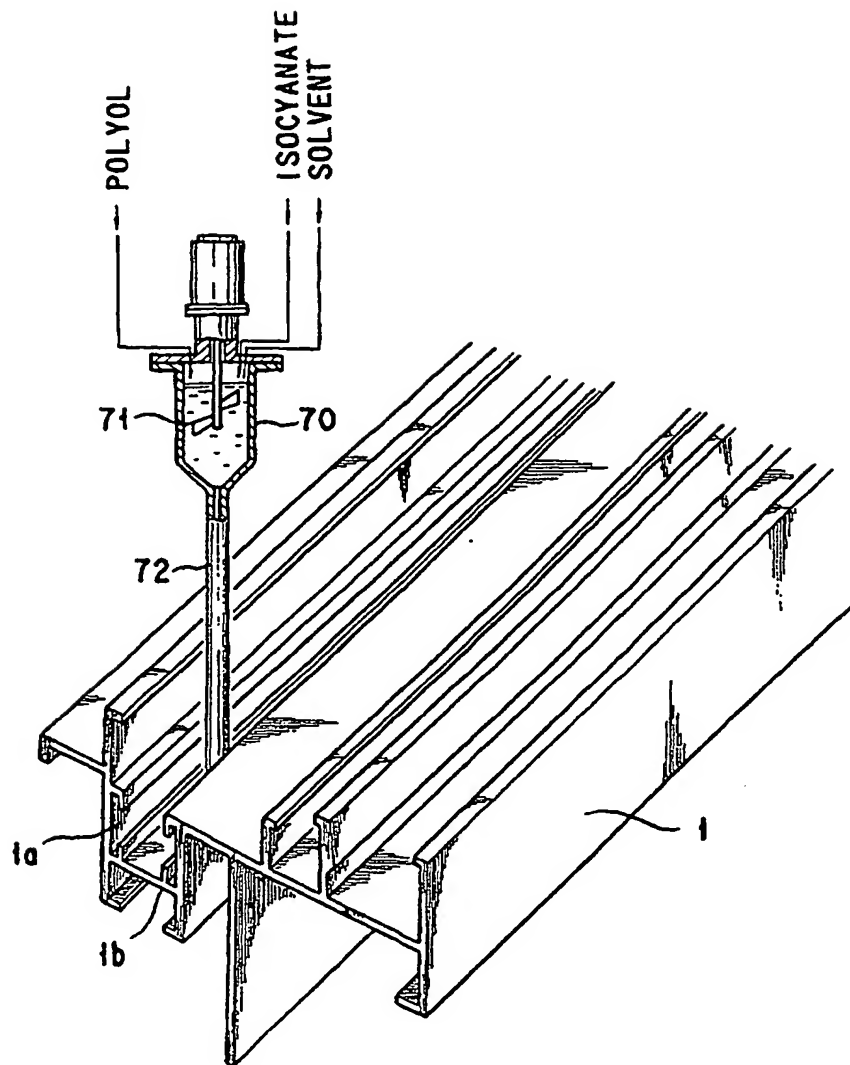


FIG. 15

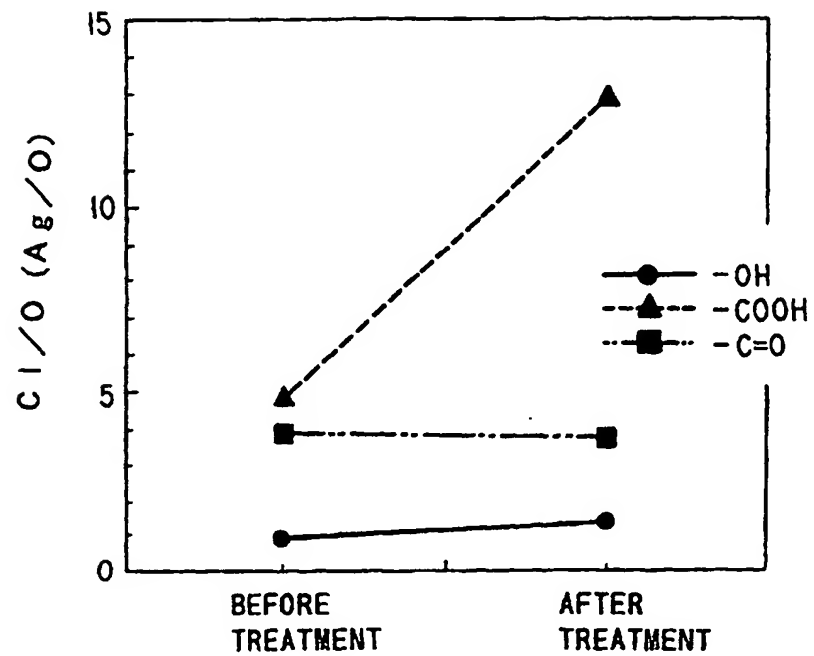


FIG. 16

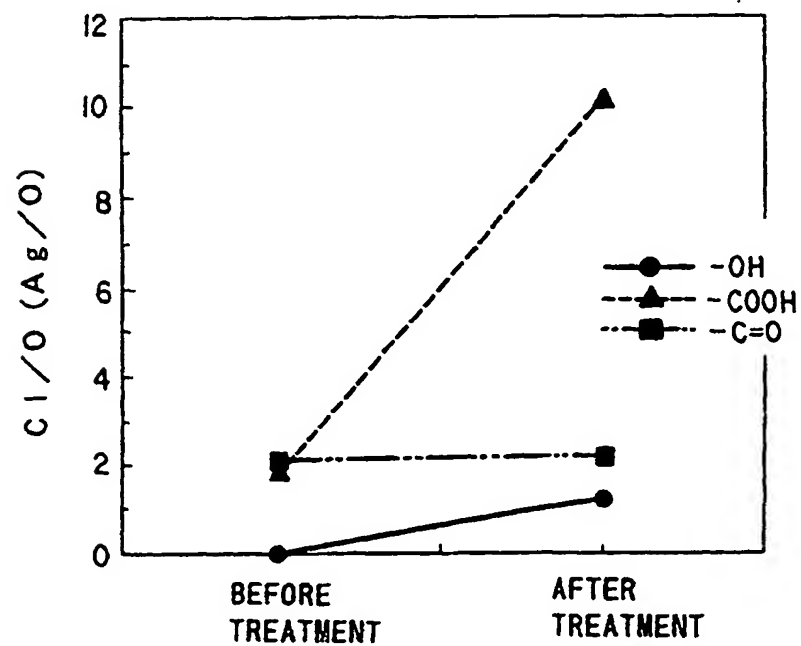


FIG. 17

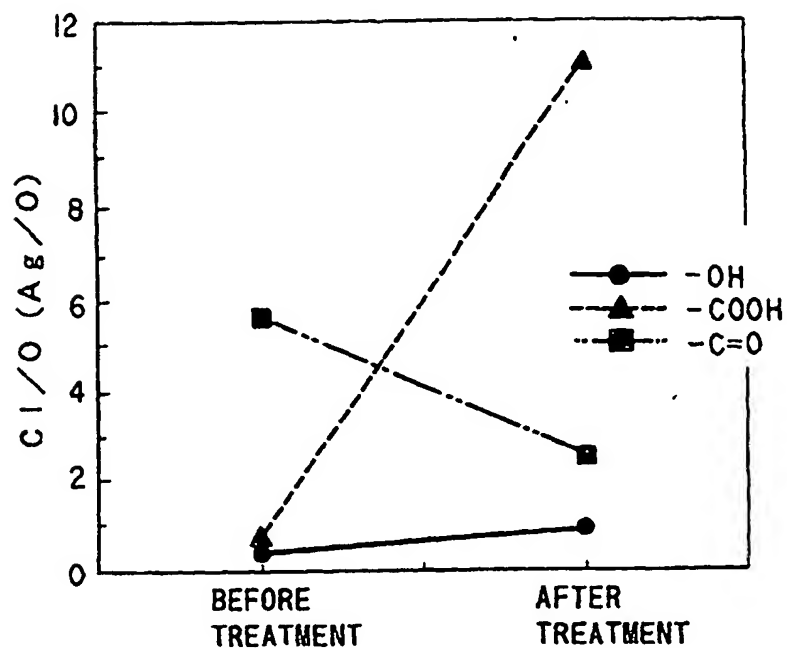
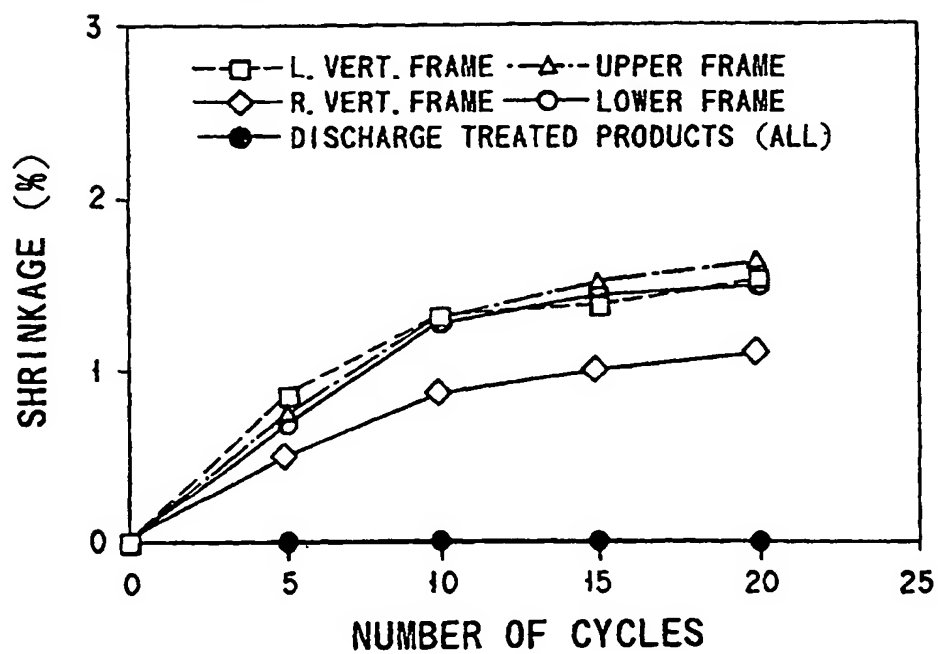
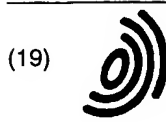


FIG. 18







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Office européen des brevets



(11) **EP 0 981 667 B9**

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- (87) International publication number:  
**WO 1998/051860 (19.11.1998 Gazette 1998/46)**

(54) **ARAGONITIC PRECIPITATED CALCIUM CARBONATE PIGMENT FOR COATING  
ROTOGRAVURE PRINTING PAPERS**

AUSGEFÄLLTES ARAGONIT KALCIUMKARBONATPIGMENT ZUR BESCHICHTUNG VON  
TIEFDRUCKPAPIEREN

UTILISATION D'UN PIGMENT DE CARBONATE DE CALCIUM ARAGONITIQUE PRECIPITE POUR  
LE COUCHAGE DE PAPIERS D'IMPRESSION A ROTOGRAVURE

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**EP 0 981 667 B9**

**Description****FIELD OF THE INVENTION**

5 [0001] The present invention is directed to a precipitated calcium carbonate pigment that has been found to be useful in the production of high quality coated paper designed for use in rotogravure printing. The precipitated calcium carbonate is preferably aragonitic in nature, and displays a high length-to-width or aspect ratio and a multimodal particle size distribution. When used in coating formulations alone or in combination with clay, talc or clay/talc blends, the carbonate of the invention provides improvement in missing dot performance when compared to typical coating grade carbonates, and is particularly advantageous in the production of lightweight coated (LWC) rotogravure papers.

**BACKGROUND OF THE INVENTION**

15 [0002] At present, three methods are used extensively for the commercial application of printing ink to paper, i.e., offset, letterpress (and flexography), and gravure type printing. In offset printing, the printing plate has hydrophilic or "water-loving" non-printing areas and hydrophobic or "water-hating" printing areas, and is "planographic", i.e., the hydrophilic and hydrophobic areas of the plate all lie in the same plane, so that the plate has no relief. During printing, the printing plate does not come in direct contact with the paper to be printed, but rather transfers the inked image to a rubber blanket, which then applies the image to paper. Therefore, the process is an indirect, or offset method, and, hence, the name offset printing. The offset printing plate is initially wetted with an aqueous-based fountain solution that is preferentially adsorbed by the hydrophilic portion of the plate, and rejected by the hydrophobic portion. The plate is then contacted with a rubber roller laden with printing ink, which is rejected by the hydrophilic regions of the plate and accepted by the hydrophobic regions.

25 [0003] A significant advantage of offset printing is the ability to adequately print on relatively rough paper, due to the use of the rubber printing blanket, which is compressible, and, thus, allows intimate contact between the printing ink and the surface of the paper. Commonly used pigments in the coatings of paper used in offset printing include calcium carbonate and clay.

[0004] Letterpress and flexography are relief printing methods, in which the inked image portion of the plate is raised compared to the surrounding non-inked portion of the plate. Letterpress is typically a direct printing method, where the plate comes in direct contact with the paper. The high cost of the engravings required to produce the letterpress printing plate is a serious limitation of this process.

35 [0005] Gravure printing is an intaglio method, in which the image area contains recessed cells that are etched into a metallic printing plate to hold the printing ink. Ink is applied to the plate, filling the cells, where the amount of ink contained in each cell is determined by the depth of the cell. After the ink is applied to the gravure plate, the plate is wiped by a doctor blade that removes ink from the smooth, flat, non-image areas. In the most common form of gravure printing, a continuous roll or web of paper is printed, hence the name rotogravure. Although the cost of preparing a gravure printing plate or cylinder is much higher than preparing an offset printing plate, a rotogravure print run is typically very long, which offsets the cost of producing the gravure printing plate.

40 [0006] Since rotogravure is a direct printing method, the best results are obtained when the paper readily drains ink from the recessed cells without an excessive amount of pressure between the paper and the printing plate. Therefore, to obtain an acceptable rotogravure print, paper with the proper ink adsorption properties and good smoothness is required. A smooth and compressible paper is required to provide proper contact between the paper surface and the cell, so that each gravure cell in the printing plate is properly drained. Where contact between the paper surface and a cell is poor, the cell is not properly drained, resulting in a problem known as "missing dots". Therefore, the need for very smooth paper is a major limitation of rotogravure printing.

45 [0007] Good smoothness is typically achieved in paper for rotogravure printing by what is known in the art as "fiber coverage". In North American rotogravure formulations, fiber coverage is generally obtained by the use of large, platy clays, such as delaminated clay, to form a structure that bridges fibers in the paper. In Europe, talc is commonly used as an effective bridging pigment. Fiber coverage can also be enhanced with the use of structuring pigments, such as calcined clay, which improve the bulk of the coating, and can also improve compressibility.

50 [0008] Carbonates have rarely been used in rotogravure papers for a number of reasons, including high missing dots, increased roughness, and low gloss. In addition, most LWC rotogravure papers are still made by an acid papermaking process, and the carbonate, when used as a filler, will decompose in the acidic media used in the acid papermaking process. As a result, the acid papermaking process can tolerate only very small quantities of carbonate without experiencing serious processing problems. Therefore, even though calcium carbonate may be used as a coating pigment, where exposure to acidic conditions is limited, the teaching of the prior art has generally been that carbonates should not be used in rotogravure papers.

RELATED ART

[0009] U.K. Patent Application GB 2139606 discloses a calcium carbonate coating pigment that contains 50 to 70 percent by weight of particles smaller than 1  $\mu\text{m}$ , less than 10 percent of the particles smaller than 0.2  $\mu\text{m}$ , and a BET specific surface area of less than 10  $\text{m}^2/\text{g}$  for use as a high-solids coating pigment for gravure papers. The preferred particles are ground, and have a shape consistent with ground calcium carbonate.

[0010] However, U.S. Patent No. 5,120,365 teaches that the calcium carbonate pigment disclosed in DE-OS P 33 16 949.7, the priority document for U.K. Patent Application GB 2139606, has not established itself in practice for use in rotogravure printing because the number of missing dots is too great, and the gloss of the paper is too low. U.S. Patent No. 5,120,365 also teaches that typical rotogravure coatings clays, such as kaolin and "Superclay", an English kaolin, are very good for printability purposes, but have poor rheological behavior, higher binder requirements, can only be worked in low solids applications, and provide low gloss.

[0011] U.S. Patent No. 5,120,365 discloses a pigment mixture that contains 40 to 80 percent by weight calcium carbonate and/or dolomite and 20 to 60 percent by weight talc, a talc-kaolin mixture, or a talc-mica mixture, where 50 to 80 percent by weight of the talc in the talc-kaolin or talc-mica mixture has a particle size distribution of 98 to 100 percent less than 20  $\mu\text{m}$ , 25 to 70 percent less than 2  $\mu\text{m}$ , 12 to 40 percent less than 1  $\mu\text{m}$ , and 0.1 to 12 percent less than 0.2  $\mu\text{m}$ , and a calcium carbonate or dolomite particle size distribution of 95 to 100 percent less than 10  $\mu\text{m}$ , 60 to 98 percent less than 2  $\mu\text{m}$ , 15 to 80 percent less than 1  $\mu\text{m}$ , and 0.1 to 20 percent less than 0.2  $\mu\text{m}$ , where the size of the particle corresponds to a spherical diameter. Fiber coverage is provided by increasing the application solids level of the carbonate-containing coating. Improved smoothness is a well-known effect of a higher solids application.

[0012] GB 2139606 and U.S. 5,120,365 also cite two publications that strongly advise against the use of calcium carbonate as a coating pigment for use in rotogravure papers:

1) Dr. Ken Beazley, How Developments in Coating Pigments Affect Paper Printability, ECC International, an in-house periodical, 1981, pages 1 and 2, states that ground calcium carbonate is a poorer coating pigment than kaolin clay for rotogravure papers, and stresses that calcium carbonate gives poor printability.

2) Possibilities and Limitations of High Solids Colors, 1979 TAPPI Coating Conference Proceedings, page 39, states that the print quality is poorer when using ground calcium carbonate than when using kaolin at the same or higher solids concentration.

[0013] U.S. Patent No. 5,478,388 teaches in a first aspect a paper coating pigment, comprising (a) from 10 percent to 100 percent by weight of a first paper coating pigment having a particle size distribution such that at least 75 percent by weight of the particles have an equivalent spherical diameter smaller than 2  $\mu\text{m}$ , and at least 60 percent have an equivalent spherical diameter smaller than 1  $\mu\text{m}$ , where the average particle aspect ratio of the fraction having an equivalent spherical diameter predominately smaller than 1  $\mu\text{m}$  is 25:1 or greater, preferably, 40:1 or greater, and (b) up to 90 percent by weight of a second coating pigment.

[0014] In a second aspect, U.S. Patent No. 5,478,388 teaches a paper coating pigment having a particle size distribution such that at least 45 percent by weight of the particles have an equivalent spherical diameter smaller than 2  $\mu\text{m}$ , and a distribution of particle aspect ratios such that if the pigment is subjected to a particle size separation to divide the pigment into a first fraction consisting of particles having an equivalent spherical diameter predominately larger than 1  $\mu\text{m}$  and a second fraction having an equivalent spherical diameter predominately smaller than 1  $\mu\text{m}$ , the average aspect ratio of each fraction is greater than 25:1.

[0015] In a third aspect, U.S. Patent No. 5,478,388 teaches a method for enhancing the water retention and/or improving the high speed runnability of a paper coating composition, comprising the step of substantially increasing the average aspect ratio of the size fraction of the paper coating pigment smaller than 1  $\mu\text{m}$ .

[0016] EP-A-768344 relates to the use of aragonitic precipitated calcium carbonate for paper coating.

[0017] There still remains a need for improved coating grade calcium carbonate pigments for rotogravure printing paper.

## SUMMARY OF THE INVENTION

[0018] The present invention relates to paper coated with a coating pigment which comprises aragonitic precipitated calcium carbonate (PCC) particles having an aspect ratio of from about 3:1 to about 15:1; preferably from about 4:1 to about 7:1, and a multimodal particle size distribution, which is preferably bimodal or trimodal. The aragonitic precipitated calcium carbonate is present in an amount from about 20 to about 100 percent weight. The coated paper of the present invention is particularly useful in rotogravure printing.

[0019] The present invention also relates to a method for preparing the coated paper, which comprises preparing the aragonitic PCC pigment and applying the pigment to the paper basestock.

[0020] The modality of the particle size distribution of the aragonitic PCC is such that from about 0 (zero) percent to about 25 percent of the particles have an equivalent spherical diameter of less than about 0.4  $\mu\text{m}$ , from about 40 percent to about 60 percent of the particles have an equivalent spherical diameter of from about 0.4  $\mu\text{m}$  to about 1.0  $\mu\text{m}$ , from about 10 percent to about 35 percent of the particles have an equivalent spherical diameter of from about 1  $\mu\text{m}$  to about 3  $\mu\text{m}$ , and from about 0 (zero) percent to about 20 percent of the particles have an equivalent spherical diameter of from about 3  $\mu\text{m}$  to about 10  $\mu\text{m}$ . Preferably, the modality is such that from about 5 percent to about 15 percent of the particles have an equivalent spherical diameter of less than about 0.4  $\mu\text{m}$ , from about 45 percent to about 55 percent of the particles have an equivalent spherical diameter of from about 0.4  $\mu\text{m}$  to about 1.0  $\mu\text{m}$ , from about 25 percent to about 35 percent of the particles have an equivalent spherical diameter of from about 1  $\mu\text{m}$  to about 3  $\mu\text{m}$ , and from about 5 percent to 10 percent of the particles have an equivalent spherical diameter of from about 3  $\mu\text{m}$  to about 10  $\mu\text{m}$ . Another preferable modality is one in which from about 15 percent to about 25 percent of the particles have an equivalent spherical diameter of less than about 0.4  $\mu\text{m}$ , from about 55 percent to about 65 percent of the particles have an average equivalent spherical diameter of from about 0.4  $\mu\text{m}$  to about 1  $\mu\text{m}$ . From about 10 percent to about 20 percent of the particles have an equivalent spherical diameter of from about 1  $\mu\text{m}$  to about 3  $\mu\text{m}$ , and from about 0 (zero) percent to about 10 percent of the particles have an equivalent spherical diameter of from about 3  $\mu\text{m}$  to about 10  $\mu\text{m}$ .

[0021] Typically, the precipitated calcium carbonate has a specific surface area of from about 4  $\text{m}^2/\text{g}$  to about 15  $\text{m}^2/\text{g}$ , and an overall particle size distribution such that substantially all of the particles, i.e., about 100 percent, have an equivalent spherical diameter of less than about 15  $\mu\text{m}$ , from about 70 percent to about 95 percent of the particles have an equivalent spherical diameter of less than about 2  $\mu\text{m}$ , from about 50 percent to about 85 percent of the particles have an equivalent spherical diameter of less than about 1  $\mu\text{m}$ , and less than 35 percent of the particles have an equivalent spherical diameter of less than about 0.4  $\mu\text{m}$ . Preferably, the precipitated calcium carbonate has a specific surface area of from about 5  $\text{m}^2/\text{g}$  to about 7  $\text{m}^2/\text{g}$ , and an overall particle size distribution such that substantially all of the particles have an equivalent spherical diameter of less than about 8  $\mu\text{m}$ , from about 75 percent to 85 percent of the particles have an equivalent spherical diameter of less than about 2  $\mu\text{m}$ , from about 55 percent to 80 percent of the particles have an equivalent spherical diameter of less than about 1  $\mu\text{m}$ , and less than about 15 percent of the particles have an equivalent spherical diameter of less than about 0.4  $\mu\text{m}$ . Another preferable precipitated calcium carbonate is one which has a specific surface area of from about 6  $\text{m}^2/\text{g}$  to about 8  $\text{m}^2/\text{g}$  and an overall particle size distribution such that substantially all of the particles have an average equivalent spherical diameter of less than about 8  $\mu\text{m}$ , from about 85 percent to about 95 percent of the particles have an equivalent spherical diameter of less than about 2  $\mu\text{m}$ , from about 75 percent to 85 percent of the particles have an equivalent spherical diameter of less than about 1  $\mu\text{m}$ , and less than about 25 percent of the particles have an equivalent spherical diameter of less than about 0.4  $\mu\text{m}$ .

[0022] Precipitated calcium carbonate pigments of the invention may also be used with titanium oxide, talc, calcined clay, satin white, plastic pigments, aluminum trihydrate, mica, or mixtures thereof. Other useful additives include from about 5 percent to about 10 percent by weight of a synthetic latex binder, such as a styrene/butadiene or acrylic binder, from about 2 percent to about 5 percent of a starch cobinder, from about 0.1 percent to about 1.5 percent of thickener such as carboxymethyl cellulose, hydroxymethyl cellulose, or polyacrylates, up to about 0.5 percent by weight of a starch insolubilizer, such as a melamine/formaldehyde resin, and from about 0.5 percent to about 1.5 percent by weight of a calcium stearate lubricant.

#### BRIEF DESCRIPTION OF THE DRAWING

[0023]

Figure 1 is a graph of mass population v. diameter, showing the multimodal size distribution of the particles of an aragonitic precipitated calcium carbonate for use in the coating pigment of the invention.

#### DETAILED DESCRIPTION OF THE INVENTION

[0024] Unless otherwise specified, all reference to parts or percent herein refer to percent by weight.

[0025] The present invention is directed to a high quality coated paper for rotogravure printing. The calcium carbonate is aragonitic, i.e., the orthorhombic form of crystalline calcium carbonate, and displays a high length-to-width or aspect ratio of from about 3:1 to about 15:1, preferably from about 4:1 to about 7:1, and a multimodal particle size distribution. Although, aragonitic precipitated calcium carbonates having a bimodal particle size distribution are useful in the coating pigments of the invention, the particle size distribution is preferably at least bimodal or trimodal. When used in pigment formulations alone or in combination with clay, talc or blends of clay and talc, the precipitated calcium carbonate pigment of the invention provides improvement in missing dot performance, when compared to typical prior art coating grade carbonates, and is particularly advantageous in the production of lightweight coated (LWC) rotogravure papers.

[0026] The unique combination of the aragonitic particle shape and multimodal particle size distribution of the aragonitic precipitated calcium carbonate pigment of the invention provides fiber coverage and associated rotogravure printability. Although a narrow particle size distribution may provide good fiber coverage, as determined by smoothness measurements, a series of tests have unexpectedly shown that a narrow particle size distribution alone is not sufficient to optimize missing dot performance. The aragonitic precipitated calcium carbonate pigment of the present invention provides missing dot performance because the unique multimodal distribution of the pigments provides coating bulk, compressibility, and smoothness, while the high aspect ratio provides bridging of fibers leading to increased levelness and smoothness. These factors combine to result in improved missing dot performance, meeting or exceeding the performance of typical clay- and talc-based rotogravure formulations.

[0027] In addition, the precipitated calcium carbonate pigment of the present invention has other clear advantages over clay, talc, and typical ground and non-aragonitic precipitated calcium carbonate rotogravure pigments in formulation, application, finishing, physical properties, and printability.

[0028] During formulation, the aragonitic precipitated calcium carbonate pigment of the present invention provides for easier makedown, including co-dispersion with dry talc, a lowering of Brookfield and/or Hercules viscosity, the production of higher solids coatings, and more efficient drying. Application of the coating is improved as a result of lower coating viscosities, which allow the application of higher solids coatings. The improved opacity which results from such coatings allows the elimination of calcined clay from the formulation, thereby improving blade cleanliness.

[0029] For finishing, the precipitated calcium carbonate pigment of the present invention provides for improved opacity, allowing the reduction or elimination of titanium dioxide,  $\text{TiO}_2$ , in the coating. Titanium dioxide, a common ingredient in coating formulations, is a particularly difficult pigment to "glue-down" due to its small size. The poor adhesion of  $\text{TiO}_2$  with the low levels of binder used in rotogravure grades can result in  $\text{TiO}_2$  "milking" on the supercalender. In addition, supercalender speed may be increased or the pressure may be decreased with the pigment of the invention due to a glossability that is superior to ground calcium carbonate.

[0030] Improvements in paper properties include increased opacity due to the generation of an open coating structure that can efficiently scatter light and increased brightness due both to an inherently higher brightness in the material and increased light scattering. The improved optical performance allows for the reduction or elimination of calcined clay,  $\text{TiO}_2$  and/or optical brighteners, resulting in a reduction in the cost of the coating.

[0031] The papers coated with the pigment of the invention provide improved missing dot performance, the ability to control coating structure pore size by choice of particle size for optimum printing performance, increased porosity, and, when the aragonitic precipitated calcium carbonate pigment of the invention is blended with talc, the ability to control the papers' coefficient of friction to provide fuller, usage of paper on large rotogravure reels.

[0032] Improved coating results are obtained with the aragonitic precipitated calcium carbonate pigment of the invention, either alone or in blends with clay and/or talc. The precipitated calcium carbonate content of the pigment can range from about 20 percent to about 100 percent of the coating formulation. Other pigments such as  $\text{TiO}_2$ , calcined clay, satin white, plastic pigments, aluminum trihydrate, mica or other typical inorganic pigments can be utilized at lower levels to impart particular qualities to the coated paper, such as brightness or opacity.

[0033] The pigment mixture of the invention is particularly advantageous for use in rotogravure printing papers, and may additionally contain from about 5 percent to about 10 percent by weight (dry basis, based on 100 parts dry inorganic pigment) of a synthetic latex binder, preferably of the styrene/butadiene or acrylic type, which may also contain starch as a co-binder in the range of from about 2 percent to about 5 percent.

[0034] Typically, the pigment mixture additionally contains from about 0.5 percent to about 1.5 percent calcium stearate as a lubricant. Starch-containing formulations may also contain up to about 0.5 percent of a starch insolubilizer, such as a melamine/formaldehyde resin or other typical insolubilizer. The coating can also contain dilution water in an amount needed to bring the final moisture content of the coatings to a range of from about 50 percent to about 65 percent. The coating may also contain from about 0.1 percent to about 1.5 percent of thickener such as carboxymethyl cellulose, hydroxyethyl cellulose, or polyacrylates.

[0035] To prepare the aragonitic precipitated calcium carbonate of the invention, a milk of lime ( $\text{Ca}(\text{OH})_2$ ) slurry or slake is prepared by adding water to calcium oxide ( $\text{CaO}$ ) with agitation. Preferably, about ten parts water having a temperature of at least about  $40^\circ\text{C}$ . (Centigrade) is added to one part  $\text{CaO}$  to produce a slake having a solids content of about 11 percent, based on the weight of  $\text{Ca}(\text{OH})_2$  in the solution. The slake is screened to remove grit, typically with a screen that will remove grit of about +60 mesh, and the slake temperature is adjusted to about  $50^\circ\text{C}$ . Dry aragonite, such as M60 Aragonite from the Mississippi Lime Company, located in St. Genevieve, Missouri, is added, and the slake is agitated for about 15 minutes. Preferably, the amount of aragonite added is equivalent to about five percent of the total amount of precipitated calcium carbonate that will be produced from the slake. Carbon dioxide gas is then added with vigorous agitation. The gas stream rate should be sufficient to convert substantially all of the  $\text{Ca}(\text{OH})_2$  to  $\text{CaCO}_3$  in about three hours, forming a precipitated calcium carbonate slurry of about 14 percent solids. Carbonation is complete when the pH falls to 7, at which time the carbon dioxide ( $\text{CO}_2$ ) stream is terminated. Typically, between about 9  $\text{ft}^3$  (13.17  $\text{m}^3$ ) and 10  $\text{ft}^3$  (3.53  $\text{m}^3$ ) of  $\text{CO}_2$  are required for each kilogram of precipitated calcium

carbonate produced. The product can then be dewatered to a concentration of about 70 percent solids to produce a cake that can be treated with a typical dispersant, e.g., sodium polyacrylate, and dispersed on a flat-blade or similar dispersion unit.

[0036] Data from a Sedigraph of a sample of the aragonitic precipitated calcium carbonate of the invention are shown graphically in Figure 1 in which the mass percent of particles within a given size interval is plotted against equivalent spherical diameter. The multimodal particle size distribution is clearly seen in the three substantially distinct peaks on the graph, which are centered at about 0.6  $\mu\text{m}$ , about 2  $\mu\text{m}$ , and at about 5  $\mu\text{m}$  with the majority of the particles in the range of about 0.6  $\mu\text{m}$ . The modality of the particle size distribution of the precipitated calcium carbonate measured to obtain the data in Figure 1 is such that about 7.3 percent of the particles have an equivalent spherical diameter of less than about 0.4  $\mu\text{m}$ , 51.4 percent of the particles have an equivalent spherical diameter of about 0.4  $\mu\text{m}$  to about 1.0  $\mu\text{m}$ , 21.8 percent of the particles have an equivalent spherical diameter of about 1  $\mu\text{m}$  to about 3  $\mu\text{m}$ , and 18.5 percent of the particles have an equivalent spherical diameter of from about 3  $\mu\text{m}$  to about 10  $\mu\text{m}$ . Generally, the modality of the particle size distribution of a precipitated calcium carbonate of the invention is such that from about 0 (zero) percent to about 25 percent, preferably from about 5 percent to about 15 percent, of the particles have an equivalent spherical diameter of less than about 0.4  $\mu\text{m}$ , from about 40 percent to about 60 percent, preferably from about 45 percent to about 55 percent, of the particles have an equivalent spherical diameter of from about 0.4  $\mu\text{m}$  to about 1.0  $\mu\text{m}$ , from about 15 percent to about 35 percent, preferably from about 25 percent to about 35 percent, of the particles have an equivalent spherical diameter of from about 1  $\mu\text{m}$  to about 3  $\mu\text{m}$ , and from about 0 (zero) percent to about 20 percent, preferably from about 5 percent to 10 percent, of the particles have an equivalent spherical diameter of from about 3  $\mu\text{m}$  to about 10  $\mu\text{m}$ . Another preferable modality is one in which from about 15 percent to about 25 percent of the particles have an equivalent spherical diameter of less than about 0.4  $\mu\text{m}$ , from about 55 percent to about 65 percent of the particles have an average equivalent spherical diameter of from about 0.4  $\mu\text{m}$ , to about 1  $\mu\text{m}$ . From about 10 percent to about 20 percent of the particles have an equivalent spherical diameter of from about 1  $\mu\text{m}$  to about 3  $\mu\text{m}$ , and from about 0 (zero) percent to about 10 percent of the particles have an equivalent spherical diameter of from about 3  $\mu\text{m}$  to about 10  $\mu\text{m}$ .

[0037] The overall particle size distribution of the aragonitic precipitated calcium carbonate useful in the pigment of the invention, as measured with a sedimentation technique, is such that substantially all of the particles have an equivalent spherical diameter of less than about 15  $\mu\text{m}$ , from about 70 percent to about 95 percent of the particles have an equivalent spherical diameter of less than about 2  $\mu\text{m}$ , from about 50 percent to about 85 percent of the particles have an equivalent spherical diameter of less than about 1  $\mu\text{m}$ , and less than 35 percent of the particles have an equivalent spherical diameter of less than about 0.4  $\mu\text{m}$ . Preferably, the overall particle size distribution of the aragonitic precipitated calcium carbonate is such that substantially all of the particles have an equivalent spherical diameter of less than about 8  $\mu\text{m}$ , from about 75 percent to 85 percent of the particles have an equivalent spherical diameter of less than about 2  $\mu\text{m}$ , from about 55 percent to 80 percent of the particles have an equivalent spherical diameter of less than about 1  $\mu\text{m}$ , and less than about 15 percent of the particles have an equivalent spherical diameter of less than about 0.4  $\mu\text{m}$ . Another preferable precipitated calcium carbonate is one which has a specific surface area of from about 6  $\text{m}^2/\text{g}$  to about 8  $\text{m}^2/\text{g}$  and an overall particle size distribution such that substantially all of the particles have an average equivalent spherical diameter of less than about 8  $\mu\text{m}$ , from about 85 percent to about 95 percent of the particles have an equivalent spherical diameter of less than about 2  $\mu\text{m}$ , from about 75 percent to 85 percent of the particles have an equivalent spherical diameter of less than about 1  $\mu\text{m}$ , and less than about 25 percent of the particles have an equivalent spherical diameter of less than about 0.4  $\mu\text{m}$ .

[0038] Typically, the aspect ratio of the precipitated calcium carbonate particles ranges from about 3:1 to about 15:1, preferably from about 4:1 to about 7:1, and the specific surface area ranges from about 4  $\text{m}^2/\text{g}$  to about 15  $\text{m}^2/\text{g}$ , preferably from about 5  $\text{m}^2/\text{g}$  to about 7  $\text{m}^2/\text{g}$ .

#### EXAMPLES

[0039] The following non-limiting examples are merely illustrative of the preferred embodiments of the present invention, and are not to be construed as limiting the invention, the scope of which is defined by the appended claims.

[0040] In the following examples, the aragonitic precipitated calcium carbonate of the invention is produced from a milk of lime ( $\text{Ca}(\text{OH})_2$ ) slurry (slake) prepared by adding water to calcium oxide ( $\text{CaO}$ ) using mechanical agitation. Preferably, about ten parts water having a temperature of at least 40°C. (Centigrade) is added to one part  $\text{CaO}$  to produce a slake having a solids content of about 11 percent based on the weight of the  $\text{Ca}(\text{OH})_2$  in the slurry. The slake is screened to remove grit, typically with a screen that will remove grit of about +60 mesh, and the slake temperature is adjusted to about 50°C. Dry aragonite, such as M60 Aragonite from the Mississippi Lime Company, located in St. Genevieve, Missouri, is then added, and the slake is stirred for about 15 minutes. Preferably, the amount of aragonite added is equivalent to about five percent of the total amount of precipitated calcium carbonate that will be produced from the slake. Carbon dioxide ( $\text{CO}_2$ ) gas is then introduced into the slake while vigorously agitating the

5 mixture. The CO<sub>2</sub> rate should be sufficient to convert substantially all of the Ca(OH)<sub>2</sub> to CaCO<sub>3</sub> in about three hours, forming a precipitated calcium carbonate slurry of about 14 percent solids. Carbonation is complete when the pH falls to 7, at which time the CO<sub>2</sub> introduction is terminated. Typically, between about 9 ft<sup>3</sup> (3.17 m<sup>3</sup>) and 10 ft<sup>3</sup> (3.53m<sup>3</sup>) of CO<sub>2</sub> are required for each kilogram of precipitated calcium carbonate produced. The product is then dewatered to a concentration of about 70 percent solids to produce a cake that can be treated with a typical dispersant, e.g., sodium polyacrylate and is then dispersed on a flat-blade or similar dispersion unit.

#### EXAMPLE 1

10 [0041] A typical clay control containing 90 parts of delaminated clay and 10 parts of calcined clay was prepared using a binder containing 7 parts styrene/butadiene latex, 3 parts hydroxyethylated starch, and 1 part calcium stearate lubricant. In the experimental formulations, 30 parts of a precipitated calcium carbonate were used to replace all of the calcined clay and 20 parts of delaminated clay of a typical coating pigment mixture. Each precipitated calcium carbonate pigment formulation contained the same binder. PCC-1 differs from PCC-2 and PCC-3 in that it exhibits a multimodal particle size distribution and high aspect ratio that are not found in PCC-2 and PCC-3. PCC-2 and PCC-3 are precipitated calcium carbonates, that are more blocky in particle shape and have narrower particle size distributions than the aragonitic precipitated calcium carbonate of the invention.

15 [0042] PCC-2 is an aragonitic precipitated calcium carbonate that has a unimodal size distribution, an aspect ratio of from about 1:1 to about 2:1, and an average particle size of about 0.4 μm. PCC-3 is a precipitated calcite that is blocky in nature, has a unimodal particle size distribution and an aspect ratio of from about 1:1 to about 2:1. In contrast, PCC-1 is an aragonitic precipitated calcium carbonate pigment according to the invention, having a trimodal particle size distribution similar to that shown in Figure 1 and an aspect ratio of from about 4:1 to about 7:1.

20 [0043] Pigment coatings were formulated at approximately 60 percent solids, and tested for percent solids and water retention character as determined by the AA-GWR method (Kaltex Scientific, USA). Scattering coefficients were obtained by drawing a coating film down over an impervious, smooth black glass background, and measuring the coat weight and reflectance of the film at 580 nanometers. Low shear viscosities in centipoise were measured at 10, 20, 50 and 100 revolutions per minute (rpm) using a Brookfield model RVT viscometer. High shear viscosity measurements were made using a Hercules high shear viscometer from Kaltex Scientific, USA. The Hercules viscosities were run using the following conditions: E bob, 400,000 dyne-cm/cm spring constant, 0-4400 rpm, room temperature. The formulation data for the coatings are provided in Table 1.

TABLE 1

		Clay Control	PCC-1*	PCC-2	PCC-3
35	percent solids:	60.0	58.6	60.4	60.0
	AA-GWR: (M <sup>2</sup> /g)	116	157	111	130
	Scattering coefficient (cm <sup>2</sup> /g)	921	1015	764	941
40	Brookfield viscosity				
	10:	4180	1340	1980	2280
	20:	2430	840	1160	1370
	50:	1236	462	612	720
45	100:	796	292	390	468
	Hercules viscosity: (cps)	49.3	35.4	34.0	31.9

\* - Aragonitic precipitated calcium carbonate according to the invention.

50 [0044] The pigment coatings described above were applied to a 27 pounds per ream (40 g/m<sup>2</sup>), groundwood-containing LWC basestock at a speed of 2200 ft/min (700 m/min.) using a Cylindrical Laboratory Coater (CLC-6000). The coat weight target was 4 pounds per ream (6 g/m<sup>2</sup>). Coated sheets were supercalendered 2 nips at 1050 pounds per linear foot (705 kg/m) and 150°F (65.5°C.) in order to impart a sheet gloss of approximately 55 points to the clay control.

55 [0045] The rotogravure printability of the coated papers was evaluated using a Heliotest missing dot method on an IGT print tester. Standard testing of the coated sheets included paper gloss, print gloss, brightness and opacity. The results of these tests are summarized in Table 2.

TABLE 2

	Clay Control	PCC-1*	PCC-2	PCC-3
Heliotest: (# of missing dots)	69	52	62	59
Print gloss:	75	74	76	76
75° Sheet gloss:	51	52	56	55
Brightness:	69.4	70.0	70.0	70.1
Opacity:	81.9	81.7	81.2	81.4
PPS-10 roughness:	1.74	1.58	1.74	1.76

\* - Aragonitic precipitated calcium carbonate pigment according to the invention.

[0046] The results of Example 1 demonstrate that the aragonitic precipitated calcium carbonate pigment of the invention provides excellent rheological properties in the coating color. Tests of the coated sheets indicate that optical properties, such as brightness, opacity and sheet gloss, obtained with precipitated calcium carbonate pigments are equivalent to those obtained with clay. However, the pigment of the invention additionally provides improved smoothness and rotogravure printability when compared to both the clay control and the non-aragonitic precipitated calcium carbonates. As an additional benefit, the use of the aragonitic precipitated calcium carbonate in the coating allows for the removal of 10 parts of calcined clay, a significant cost savings.

#### EXAMPLE 2

[0047] The performance of PCC-1 was again compared to a clay control similar to that used in Example 1. In this case, the control and experimental formulations contained 5 parts  $\text{TiO}_2$  for enhancement of opacity and brightness. [0048] In each experimental formulation, 30 parts of the precipitated calcium carbonate pigment was used, and the calcined clay was eliminated. The precipitated calcium carbonate pigments were used in systems that typically contained delaminated clay, and were also used in systems that contained a coating grade talc that has been developed for the production of rotogravure printing papers. The pigment formulations are given in Table 3.

TABLE 3

	1	2	3*	4	5	6*	7
Delaminated clay	85	35	35	35	65	65	65
Calcined clay	to	-	-	-	-	-	-
Montana talc	-	30	30	30	-	-	-
PCC-1	-	-	30	-	-	30	-
PCC-2	-	30	-	-	30	-	-
PCC-3	-	-	-	30	-	-	30
$\text{TiO}_2$	5	5	5	5	5	5	5

\* - Aragonitic precipitated calcium carbonate pigment according to the present invention.

[0049] The delaminated and calcined clays were received as dry powders. In preparing the pigment formulations, the delaminated clay was dispersed at 70 percent solids, and the calcined clay was dispersed at 50 percent solids using a conventional flat-blade (Cowles-type) mixer. The coating grade talc was dispersed on a Cowles mixer by directly adding dry talc to the precipitated calcium carbonate slurries at a 1:1 ratio at a solids level ranging from 70 to 77 percent, using 2 percent of a non-ionic EO/PO surfactant and 0.2 percent of a sodium polyacrylate dispersant.

[0050] The binder used was 7 parts styrene/butadiene latex and 3 parts hydroxyethylated starch. A hydroxyethyl cellulose thickener was used at the 0.1 part level for viscosity adjustment. Coatings were prepared at the highest possible solids level, and then diluted to approximately match the Hercules viscosity of the control. Coating formulation data for the pigments tested are given in Table 4.



TABLE 4

		1	2	3*	4	5	6*	7
percent solids:		60.0	66.0	63.0	64.1	65.2	63.3	64.0
AA-GWR (m <sup>2</sup> /g)		112	65	93	76	90	120	102
Scattering coefficient (cm <sup>2</sup> /g):		1204	1020	1082	1054	1036	1107	1158
Brookfield viscosity	10:	2460	4220	2400	3100	5560	3240	3900
	20:	1470	2840	1500	1940	3320	1980	2400
	50:	812	1556	840	1084	1740	1076	1260
	100:	526	1020	570	724	1108	712	820
Hercules viscosity: (cps)		50.0	51.4	57.0	54.9	52.1	50.0	54.9

\* - Aragonitic precipitated calcium carbonate pigment according to the present invention.

[0051] After preparation, the coatings were applied to a 27 pounds per ream (40 g/m<sup>2</sup>) groundwood-containing LWC basestock at a speed of 2200 ft/min (700 m/min.) using a Cylindrical Laboratory Coater (CLC-6000). The coat weight target was 4 pounds per ream (6 g/m<sup>2</sup>). Calendering conditions for the coated sheets were set to achieve a sheet gloss of approximately 50 points, the same as the clay control.

[0052] The rotogravure printability of the coated papers was evaluated using a Heliotest missing dot method on an IGT print tester. Standard testing of the coated sheets included paper gloss, print gloss, brightness and opacity. The coated sheet test data are given in Table 5.

TABLE 5

	1	2	3*	4	5	6*	7
Heliotest printability: (Distance to 20th dot)	45	33	50	46	34	52	30
75° Sheet gloss:	49	46	45	48	51	46	48
Brightness:	71.5	71.2	71.5	71.5	71.6	71.9	71.8
Opacity:	85.8	85.2	85.6	85.2	85.3	85.8	85.8
PPS-20 roughness	0.93	0.93	0.88	0.86	0.92	0.86	0.91

\* - Aragonitic precipitated calcium carbonate pigment according to the present invention.

[0053] As with Example 1, these data demonstrate the improved rotogravure printability that is provided by the coating pigment of the invention, and also demonstrates that the aragonitic precipitated calcium carbonate coating pigment can also be used in combination with talc and TiO<sub>2</sub> to produce sheets of superior performance in rotogravure printability.

### EXAMPLE 3

[0054] The performance of a formulation containing PCC-1 in combination with talc or coating clay was compared to that of PCC-3 with clay and to that of ground calcium carbonate (GCC) with clay. GCC is a natural ground calcite having a broad, unimodal size distribution and an aspect ratio of from about 1:1 to about 2:1. The clay used in each formulation was DB Plate delaminated clay, and the talc was Finntalc C10, a commercially available coating grade talc from Finland. The delaminated clay and talc were each received as dispersed slurries, approximately 70 percent solids for the delaminated clay and approximately 65 percent solids for the talc. Pigment formulations for Example 3 are given in Table 6.

TABLE 6

	1*	2	3*	4
Carbonate	PCC-1	GCC	PCC-1	PCC-3
Delaminated Clay	-	50	50	50
Finnish Talc	30	-	-	-
PCC-1	70	-	50	-
PCC-3	-	-	-	50
GCC	-	50	-	-

\* - Aragonitic precipitated calcium carbonate pigment according to the present invention.

[0055] Coatings were prepared at about 61.5 percent solids, and included a binder containing 6 parts styrene/butadiene latex. Coating formulation data are given in Table 7.

TABLE 7

	1*	2	3*	4
Carbonate	PCC-1	GCC	PCC-1	PCC-3
Percent solids	61.3	61.3	61.3	61.3
100 rpm Brookfield viscosity	576	690	610	484
Haake viscosity (cps)	28.0	30.4	44.1	29.8

\* - Aragonitic precipitated calcium carbonate pigment according to the present invention.

[0056] Coatings were applied to a 27 pounds per ream (40 g/m<sup>2</sup>) groundwood LWC basestock at a speed of 4000 ft/min (1200 m/min) using a pilot coater. A coat weight of approximately 6.8 pounds per ream (10 g/m<sup>2</sup>) was applied to the wire side, and paper samples were prepared with a felt side coating having coat weights of 5.4, 6.8, and 8.1 pounds per ream (8, 10, and 12 g/m<sup>2</sup>). The rotogravure printability of the coated papers was evaluated using a Heliotest missing dot method on an IGT print tester. Standard tests of the coated sheets included paper gloss, print gloss, brightness, and opacity. Data obtained for the properties of the coated sheets were plotted graphically, and data were interpolated at a coat weight of 6.8 pounds per ream from best-fit plots. The results are given in Table 8.

TABLE 8

	1*	2	3*	4
Carbonate	PCC-1	GCC	PCC-1	PCC-3
Heliotest printability: (distance to 20 <sup>th</sup> dot)	39	23	36	25
75° Sheet gloss:	53	53	58	57
Brightness:	79.2	77.1	78.6	78.9
Opacity:	90.7	89.6	91.0	91.1
PPS-5 Roughness:	1.42	1.58	1.45	1.52

\* - Aragonitic precipitated calcium carbonate pigment according to the present invention.

[0057] The results demonstrate that the aragonitic precipitated calcium carbonate coated pigment of the invention has superior printability and smoothness, when compared to a ground calcium carbonate pigment.

#### Claims

1. Paper for rotogravure printing coated with a pigment which comprises from 20 to 100 wt % of aragonitic precipitated calcium carbonate particles having an aspect ratio of from 3:1 to 15:1 and a multimodal particle size distribution such that from 0 (zero) percent to 25 percent of the particle have an equivalent spherical diameter of less than 0.4

μm, from 40 percent to 60 percent of the particles have an equivalent spherical diameter of from 0.4 μm to 1.0 μm, from 10 percent to 35 percent of the particles have an equivalent spherical diameter of from 1 μm to 3 μm, and from 0 (zero) percent to 20 percent of the particles have an equivalent spherical diameter of from 3 μm to 10 μm.

- 5     2. The paper according to Claim 1 wherein the aragonitic precipitated calcium carbonate pigment has a modality such that from 5 percent to 15 percent of the particles have an equivalent spherical diameter of less than 0.4 μm, from 45 percent to 55 percent of the particles have an equivalent spherical diameter of from 0.4 μm to 1.0 μm, from 25 percent to 35 percent of the particles have an equivalent spherical diameter of from 1 μm to 3 μm, and from 5 percent to 10 percent of the particles have an equivalent spherical diameter of from 3 μm to 10 μm.
- 10     3. The paper according to Claim 1 wherein the aragonitic precipitated calcium carbonate pigment has a modality such that from 15 percent to 25 percent of the particles have an equivalent spherical diameter of less than 0.4 μm, from 55 percent to 65 percent of the particles have an equivalent spherical diameter of from 0.4 μm to 1.0 μm, from 10 percent to 20 percent of the particles have an equivalent spherical diameter of from 1.0 μm to 3.0 μm, and from 0 (zero) percent to 10 percent of the particles have an equivalent spherical diameter of from 3 μm to 10 μm.
- 15     4. The paper according to any of the preceding Claims, wherein the aragonitic calcium carbonate has an aspect ratio of from 4:1 to 7:1.
- 20     5. The paper according to any of the preceding Claims, wherein the aragonitic precipitated calcium carbonate has a specific surface area of from 4 m<sup>2</sup>/g to 15 m<sup>2</sup>/g, and an overall particle size distribution less than 15 μm, from 70 percent to 95 percent of the particles have an equivalent spherical diameter of less than 2 μm, from 50 percent to 85 percent of the particles have an equivalent spherical diameter of less than 1 μm, and less than 35 percent of the particles have an equivalent spherical diameter of less than 0.4 μm.
- 25     6. The paper according to Claim 5 wherein the aragonitic precipitated calcium carbonate has a specific surface area of from 5 m<sup>2</sup>/g to 7 m<sup>2</sup>/g, and an overall particle size distribution of less than 8 μm, from 75 percent to 85 percent of the particles have an equivalent spherical diameter of less than 2 μm, from 55 percent to 80 percent of the particles have an equivalent spherical diameter of less than 1 μm, and less than 15 percent of the particles have an equivalent spherical diameter of less than 0.4 μm.
- 30     7. The paper according to Claim 5 wherein the aragonitic precipitated calcium carbonate has a specific surface area of from 6 m<sup>2</sup>/g to 8 m<sup>2</sup>/g, and an overall particle size distribution such that substantially all of the particles have an equivalent spherical diameter of less than 8 μm, from 85 percent to 95 percent of the particles have an equivalent spherical diameter of less than 2 μm, from 75 percent to 85 percent of the particles have an equivalent spherical diameter less than 1 μm, and less than 25 percent have an equivalent spherical diameter of less than 0.4 μm.
- 35     8. The paper according to any of the preceding Claims further comprising titanium dioxide, talc, calcined clay, satin white, plastic pigments, aluminium trihydrate, mica, or mixtures thereof.
- 40     9. The paper according to any of the preceding Claims, further comprising from 5 percent to 10 percent by weight of a synthetic latex binder.
- 45     10. The paper according to Claim 9, wherein the synthetic latex binder is a styrene/butadiene or acrylic binder.
- 50     11. The paper according to Claim 9 or Claim 10 further comprising from about 2 percent to about 5 percent of a starch co-binder.
- 55     12. The paper according to Claim 1 further comprising up to 0.5 percent by weight of a starch insolubiliser.
13. The paper according to Claim 12 wherein the starch insolubiliser is a melamine/formaldehyde resin.
14. The paper according to any of the preceding Claims, further comprising from, 0.5 percent to 1.5 percent by weight of a calcium stearate lubricant.
15. A method of preparing paper for rotogravure printing, which comprises preparing the pigment as specified in any of Claims 1 to 7 and applying a coating of the pigment to a paper basestock.

16. The use as a pigment for coating paper for rotogravure printing of calcium carbonate which comprises from 20 to 100 wt % of aragonitic precipitated calcium carbonate particles having an aspect ratio of from 3:1 to 15:1 and a multimodal particle size distribution such that from 0 (zero) present to 25 percent of the particle have an equivalent spherical diameter of less than 0.4  $\mu\text{m}$ , from 40 percent to 60 percent of the particles have an equivalent spherical diameter of from 0.4  $\mu\text{m}$  to 1.0  $\mu\text{m}$ , from 10 percent to 35 percent of the particles have an equivalent spherical diameter of from 1  $\mu\text{m}$  to 3  $\mu\text{m}$ , and from 0 (zero) percent to 20 percent of the particles have an equivalent spherical diameter of from 3  $\mu\text{m}$  to 10  $\mu\text{m}$ .

## 10 Patentansprüche

1. Papier für Tiefendruck beschichtet mit einem Pigment, welches von 20 Gew.-% bis 100 Gew.-% ausgefällte Aragonit-Kalziumkarbonatteilchen aufweist, die ein Längenverhältnis von 3:1 bis 15:1 und eine multimodale Teilchengrößenverteilung aufweisen, derart, daß 0 (null) Prozent bis 25 Prozent der Teilchen einen äquivalenten sphärischen Durchmesser von weniger als 0,4 $\mu\text{m}$  aufweisen, 40 Prozent bis 60 Prozent der Teilchen einen äquivalenten sphärischen Durchmesser von 0,4 $\mu\text{m}$  bis 1,0 $\mu\text{m}$  aufweisen, 10 Prozent bis 35 Prozent der Teilchen einen äquivalenten sphärischen Durchmesser von 1 $\mu\text{m}$  bis 3 $\mu\text{m}$  aufweisen und 0 (null) Prozent bis 20 Prozent der Teilchen einen äquivalenten sphärischen Durchmesser von 3 $\mu\text{m}$  bis 10 $\mu\text{m}$  aufweisen.
2. Papier nach Anspruch 1, wobei das ausgefällte Aragonit-Kalziumkarbonatpigment eine Modalität aufweist, derart, daß 5 Prozent bis 15 Prozent der Teilchen einen äquivalenten sphärischen Durchmesser von weniger als 0,4 $\mu\text{m}$  aufweisen, 45 Prozent bis 55 Prozent der Teilchen einen äquivalenten sphärischen Durchmesser von 0,4 $\mu\text{m}$  bis 1,0 $\mu\text{m}$  aufweisen, 25 Prozent bis 35 Prozent der Teilchen einen äquivalenten sphärischen Durchmesser von 1 $\mu\text{m}$  bis 3 $\mu\text{m}$  aufweisen und 5 Prozent bis 10 Prozent der Teilchen einen äquivalenten sphärischen Durchmesser von 3 $\mu\text{m}$  bis 10 $\mu\text{m}$  aufweisen.
3. Papier nach Anspruch 1, wobei das ausgefällte Aragonit-Kalziumkarbonatpigment eine Modalität aufweist, derart, daß 15 Prozent bis 25 Prozent der Teilchen einen äquivalenten sphärischen Durchmesser von weniger als 0,4 $\mu\text{m}$  aufweisen, 55 Prozent bis 65 Prozent der Teilchen einen äquivalenten sphärischen Durchmesser von 0,4 $\mu\text{m}$  bis 1,0 $\mu\text{m}$  aufweisen, 10 Prozent bis 20 Prozent der Teilchen einen äquivalenten sphärischen Durchmesser von 1,0 $\mu\text{m}$  bis 3,0 $\mu\text{m}$  aufweisen und 0 (null) Prozent bis 10 Prozent der Teilchen einen äquivalenten sphärischen Durchmesser von 3 $\mu\text{m}$  bis 10 $\mu\text{m}$  aufweisen.
4. Papier nach einem der vorhergehenden Ansprüche, wobei das Aragonit-Kalziumkarbonat ein Längenverhältnis von 4:1 bis 7:1 aufweist.
5. Papier nach einem der vorhergehenden Ansprüche, wobei das ausgefällte Aragonit-Kalziumkarbonat eine spezifische Oberfläche von 4 $\text{m}^2/\text{g}$  bis 15 $\text{m}^2/\text{g}$  und eine Gesamtteilchengrößenverteilung von weniger als 15 $\mu\text{m}$  aufweist, wobei 70 Prozent bis 95 Prozent der Teilchen einen äquivalenten sphärischen Durchmesser von weniger als 2 $\mu\text{m}$  aufweisen, 50 Prozent bis 85 Prozent der Teilchen einen äquivalenten sphärischen Durchmesser von weniger als 1  $\mu\text{m}$  aufweisen und weniger als 35 Prozent der Teilchen einen äquivalenten sphärischen Durchmesser von weniger als 0,4 $\mu\text{m}$  aufweisen.
6. Papier nach Anspruch 5, wobei das ausgefällte Aragonit-Kalziumkarbonat eine spezifische Oberfläche von 5 $\text{m}^2/\text{g}$  bis 7 $\text{m}^2/\text{g}$  und eine Gesamtteilchengrößenverteilung von weniger als 8 $\mu\text{m}$  aufweist, wobei 75 Prozent bis 85 Prozent der Teilchen einen äquivalenten sphärischen Durchmesser von weniger als 2 $\mu\text{m}$  aufweisen, 55 Prozent bis 80 Prozent der Teilchen einen äquivalenten sphärischen Durchmesser von weniger als 1 $\mu\text{m}$  aufweisen und weniger als 15 Prozent der Teilchen einen äquivalenten sphärischen Durchmesser von weniger als 0,4 $\mu\text{m}$  aufweisen.
7. Papier nach Anspruch 5, wobei das ausgefällte Aragonit-Kalziumkarbonat eine spezifische Oberfläche von 6 $\text{m}^2/\text{g}$  bis 8 $\text{m}^2/\text{g}$  und eine Gesamtteilchengrößenverteilung aufweist, so daß im wesentlichen alle Teilchen einen äquivalenten sphärischen Durchmesser von weniger als 8 $\mu\text{m}$  haben, wobei 85 Prozent bis 95 Prozent der Teilchen einen äquivalenten sphärischen Durchmesser von weniger als 2 $\mu\text{m}$  aufweisen, 75 Prozent bis 85 Prozent der Teilchen einen äquivalenten sphärischen Durchmesser von weniger als 1 $\mu\text{m}$  aufweisen und weniger als 25 Prozent der Teilchen einen äquivalenten sphärischen Durchmesser von weniger als 0,4 $\mu\text{m}$  aufweisen.
8. Papier nach einem der vorhergehenden Ansprüche, weiter aufweisend Titandioxid, Talkum, kalzinierter Ton, Sa-

tinweiß, Kunststoffpigmente, Aluminiumtrihydrat, Glimmer oder Mischungen aus diesen.

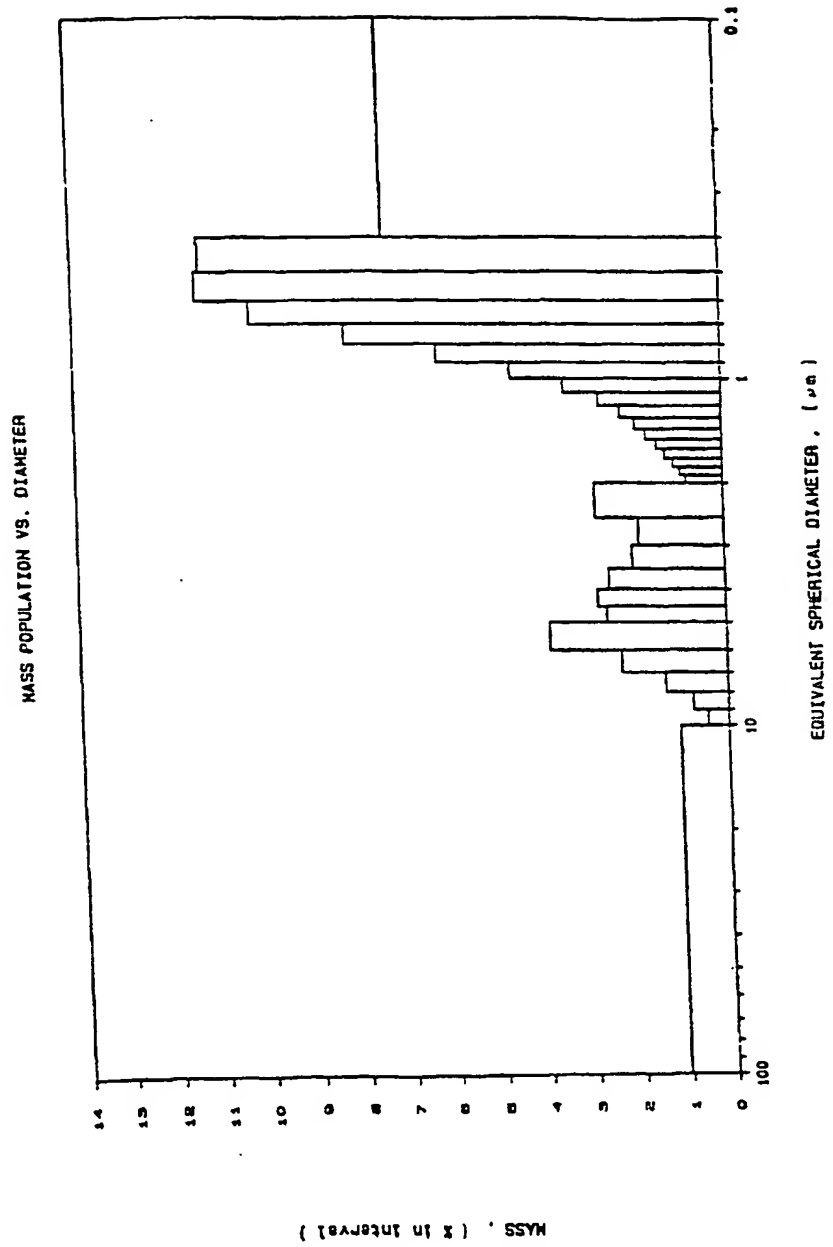
9. Papier nach einem der vorhergehenden Ansprüche, weiter aufweisend 5 Gew.-Prozent bis 10 Gew.-Prozent eines synthetischen Latexbinders.  
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10. Papier nach Anspruch 9, wobei der synthetische Latexbinder ein Styrol/Butadien oder Acrylbinder ist.
11. Papier nach Anspruch 9 oder Anspruch 10, weiter aufweisend ungefähr 2 Prozent bis ungefähr 5 Prozent eines Stärke Co-Binders.  
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12. Papier nach Anspruch 1, weiter aufweisend bis zu 0,5 Gew.-Prozent eines Stärke-Insolubilisierers,
13. Papier nach Anspruch 12, wobei der Stärke-Insolubilisierer ein Melamin/Formaldehyd Harz ist.
14. Papier nach einem der vorhergehenden Ansprüche, weiter aufweisend 0,5 Gew.-Prozent bis 1,5 Gew.-Prozent eines Kalziumstearat-Schmiermittels.  
15
15. Verfahren zur Aufbereitung von Papier für Tiefendruck, welches ein Aufbereiten des Pigments nach einem der Ansprüche 1 bis 7 und ein Anwenden einer Beschichtung aus dem Pigment auf einen Papier-Grundbestand aufweist.  
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16. Verwendung von Kalziumkarbonat als Pigment zum Beschichten von Papier für Tiefendrucke, welches von 20 Gew.-Prozent bis 100 Gew.-Prozent ausgefällte Aragonit-Kalziumkarbonatteilchen aufweist, die ein Längenverhältnis von 3:1 bis 15:1 und eine multimodale Teilchengrößenverteilung aufweisen, derart, daß 0 (null) Prozent bis 25 Prozent der Teilchen einen äquivalenten sphärischen Durchmesser von weniger als 0,4µm aufweisen, 40 Prozent bis 60 Prozent der Teilchen einen äquivalenten sphärischen Durchmesser von 0,4µm bis 1,0µm aufweisen, 10 Prozent bis 35 Prozent der Teilchen einen äquivalenten sphärischen Durchmesser von 1µm bis 3µm aufweisen und 0 (null) Prozent bis 20 Prozent der Teilchen einen äquivalenten sphärischen Durchmesser von 3µm bis 10µm aufweisen.  
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#### Revendications

1. Papier destiné à une impression par rotogravure, couché avec un pigment qui comprend de 20 à 100 % en poids de particules de carbonate de calcium précipité aragonitique présentant un rapport de dimensions de 3:1 à 15:1 et une distribution de taille de particules à mode multiple telle que de 0 (zéro) pour cent à 25 pour cent des particules présentent un diamètre sphérique équivalent inférieur à 0,4 µm, de 40 pour cent à 60 pour cent des particules présentent un diamètre sphérique équivalent de 0,4 µm à 1,0 µm, de 10 pour cent à 35 pour cent des particules présentent un diamètre sphérique équivalent de 1 µm à 3 µm, et de 0 (zéro) pour cent à 20 pour cent des particules présentent un diamètre sphérique équivalent de 3 µm à 10 µm.  
35  
40
2. Papier selon la revendication 1, dans lequel le pigment de carbonate de calcium précipité aragonitique présente un mode tel que de 5 pour cent à 15 pour cent des particules présentent un diamètre sphérique équivalent inférieur à 0,4 µm, de 45 pour cent à 55 pour cent des particules présentent un diamètre sphérique équivalent de 0,4 µm à 1,0 µm, de 25 pour cent à 35 pour cent des particules présentent un diamètre sphérique équivalent de 1 µm à 3 µm, et de 5 pour cent à 10 pour cent des particules présentent un diamètre sphérique équivalent de 3 µm à 10 µm.  
45
3. Papier selon la revendication 1, dans lequel le pigment de carbonate de calcium précipité aragonitique présente un mode tel que de 15 pour cent à 25 pour cent des particules présentent un diamètre sphérique équivalent inférieur à 0,4 µm, de 55 pour cent à 65 pour cent des particules présentent un diamètre sphérique équivalent de 0,4 µm à 1,0 µm, de 10 pour cent à 20 pour cent des particules présentent un diamètre sphérique équivalent de 1,0 µm à 3,0 µm, et de 0 (zéro) pour cent à 10 pour cent des particules présentent un diamètre sphérique équivalent de 3 µm à 10 µm.  
50
4. Papier selon l'une quelconque des revendications précédentes, dans lequel le carbonate de calcium aragonitique présente un rapport de dimensions de 4:1 à 7:1.  
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5. Papier selon l'une quelconque des revendications précédentes, dans lequel le carbonate de calcium précipité

- aragonitique présente une surface spécifique de 4 m<sup>2</sup>/g à 15 m<sup>2</sup>/g, et une distribution de taille de particules globale inférieure à 15 µm, de 70 pour cent à 95 pour cent des particules présentent un diamètre sphérique équivalent inférieur à 2 µm, de 50 pour cent à 85 pour cent des particules présentent un diamètre sphérique équivalent inférieur à 1 µm, et moins de 35 pour cent des particules présentent un diamètre sphérique équivalent inférieur à 0,4 µm.
- 5
6. Papier selon la revendication 5, dans lequel le carbonate de calcium précipité aragonitique présente une surface spécifique de 5 m<sup>2</sup>/g à 7 m<sup>2</sup>/g et une distribution de taille de particules globale inférieure à 8 µm, de 75 pour cent à 85 pour cent des particules présentent un diamètre sphérique équivalent inférieur à 2 µm, de 55 pour cent à 80 pour cent des particules présentent un diamètre sphérique équivalent inférieur à 1 µm, et moins de 15 pour cent des particules présentent un diamètre sphérique équivalent inférieur à 0,4 µm.
- 10
7. Papier selon la revendication 5, dans lequel le carbonate de calcium précipité aragonitique présente une surface spécifique de 6 m<sup>2</sup>/g à 8 m<sup>2</sup>/g et une distribution de taille de particules globale telle que pratiquement toutes les particules présentent un diamètre sphérique équivalent inférieur à 8 µm, de 85 pour cent à 95 pour cent des particules présentent un diamètre sphérique équivalent inférieur à 2 µm, de 75 pour cent à 85 pour cent des particules présentent un diamètre sphérique équivalent inférieur à 1 µm, et moins de 25 pour cent présentent un diamètre sphérique équivalent de moins de 0,4 µm.
- 15
8. Papier selon l'une quelconque des revendications précédentes, comprenant en outre du dioxyde de titane, du talc, de l'argile calcinée, du blanc satiné, des pigments de matière plastique, du trihydrate d'aluminium, du mica, ou des mélanges de ceux-ci.
- 20
9. Papier selon l'une quelconque des revendications précédentes, comprenant en outre de 5 pour cent à 10 pour cent en poids d'un liant de latex synthétique.
- 25
10. Papier selon la revendication 9, dans lequel le liant de latex synthétique est un liant de styrène/butadiène ou acrylique.
- 30
11. Papier selon la revendication 9 ou la revendication 10, comprenant en outre d'environ 2 pour cent à environ 5 pour cent d'un co-liant d'amidon.
- 35
12. Papier selon la revendication 1, comprenant en outre jusqu'à 0,5 pour cent en poids d'un agent d'insolubilisation d'amidon.
- 40
13. Papier selon la revendication 12, dans lequel l'agent d'insolubilisation d'amidon est une résine de mélamine/formaldéhyde.
- 45
14. Papier selon l'une quelconque des revendications précédentes, comprenant en outre de 0,5 pour cent à 1,5 pour cent en poids d'un lubrifiant de stéarate de calcium.
- 50
15. Procédé de préparation d'un papier en vue d'une impression par rotogravure, qui comprend la préparation du pigment telle que spécifiée selon l'une quelconque des revendications 1 à 7, et l'application d'un couchage du pigment sur un support de base de papier.
- 55
16. Utilisation en tant que pigment pour le couchage d'un papier en vue d'une impression par rotogravure de carbonate de calcium, qui comprend de 20 à 100 % en poids de particules de carbonate de calcium précipité aragonitique présentant un rapport de dimensions de 3:1 à 15:1 et une distribution de taille de particules à mode multiple telle que de 0 (zéro) pour cent à 25 pour cent des particules présentent un diamètre sphérique équivalent inférieur à 0,4 µm, de 40 pour cent à 60 pour cent des particules présentent un diamètre sphérique équivalent de 0,4 µm à 1,0 µm, de 10 pour cent à 35 pour cent des particules présentent un diamètre sphérique équivalent de 1 µm à 3 µm, et de 0 (zéro) pour cent à 20 pour cent des particules présentent un diamètre sphérique équivalent de 3 µm à 10 µm.

Figure 1



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